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ON THE NUMBERS OF WARD AND BERNOULLI.

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Received November 11, 1935.
(Communicated by Dr. S. Chowla.)

§1. Introduction. Defining $G(n, r)$ as the coefficient of x^{n-r} in the expansion of $(x+1)(x+2)(x+3)\cdots(x+n)$, I have shown[1] that

$$G(n+1, r) - G(n, r) = (n+1)\,G(n, r-1) \quad .. \quad .. \quad (1)$$

n and r being integers > 0.

Defining $G(n, r)$ for all values of n by equation (1), I have shown[2] that

$$(n-1)!\,G(-n-1, r) = n^{n+r-1} - \binom{n-1}{1}(n-1)^{n+r-1} + \binom{n-1}{2}(n-2)^{n+r-1} - \cdots + (-1)^{n-1}\binom{n-1}{n-1}\cdot 1^{n+r-1} \quad (2)$$

where n and r are integers, $n \geqslant 1$.

Professor Morgan Ward has shown[3] that

$$G(n, r) = \sum_{m=0}^{r-1}\left\{(-1)^m \cdot H(r, m)\cdot \binom{n+r-m}{2r-m}\right\}, \quad .. \quad .. \quad (3)$$

where the H's are positive integers defined recursively by

$$H(r+1, m) = (2r+1-m).\,H(r, m) + (r+1-m).\,H(r, m-1),$$

with the initial values $H(0, 0) = 1$, $H(r+1, 0) = 1.3.5.\cdots(2r+1)$.

Towards the end of his paper, Ward gives expressions for $H(r, r-m)$, $m \leqslant 5$; with two evident misprints in the last result. Hence he conjectures the form of $H(r, r-m)$. He is, however, not able to prove his statement.

In §2 of this paper, my object is to obtain a definite expression for $H(r, r-m)$. In §3, I study the action of Δ^s on $G(n, r)$. In §4, I obtain an explicit expression for $\sum_{i=1}^{n} i^s$. This result was of use to me in proving a "Generalisation of Wolstenholme's Theorem".[4] Finally, I give some expressions for Bernoulli's Numbers in §5.

§2. 1. Professor Ward's H's and θ's.

Putting $-m-1$ for n in (3), we get

$$G(-m-1, r) = H(r, r-m) + \binom{r+m}{1} H(r, r-m+1) + \binom{r+m}{2} H(r, r-m+2) + \cdots\cdots + \binom{r+m}{m-1} H(r, r-1);\ 1 \leqslant m \quad \ldots (4)$$

Giving to m in succession the values 1, 2, 3, $\cdots\cdots$, and making use of (2), we easily obtain all the five results given by Ward. In general, we get

$$H(r, r-m) = \begin{vmatrix} G(-m-1, r), & \binom{r+m}{1}, & \binom{r+m}{2}, & \cdots, & \binom{r+m}{m-1} \\ G(-m, r), & \binom{r+m-1}{0}, & \binom{r+m-1}{1}, & \cdots, & \binom{r+m-1}{m-2} \\ G(-m+1, r), & 0, & \binom{r+m-2}{0}, & \cdots, & \binom{r+m-2}{m-3} \\ \cdots, & \cdots, & \cdots, & \cdots, & \cdots \\ G(-2, r), & 0, & 0, & \cdots, & \binom{r+1}{0} \end{vmatrix} \quad \ldots (5)$$

$$= G(-m-1, r) - \binom{r+m}{1} G(-m, r) + \binom{r+m}{2} G(-m+1, r) - \cdots + (-1)^{m-1} \binom{r+m}{m-1} G(-2, r) \ldots (6)^*$$

Substituting (6) in (3), we obtain[5]

$$G(n, r) = \sum_{k=1}^{r} \left\{(-1)^{r+k} \binom{n+k}{r+k} \binom{n+r+1}{r-k} G(-k-1, r)\right\}.$$

2. 2. Multiplying the rows of the determinant in (5) by $(m-1)!$, $(m-2)!$, $(m-3)!$, $\cdots$, $0!$, in order from top to bottom, and dividing the columns by 1, $(m-2)!$, $(m-3)!$, $\cdots$, $0!$, in order from left to right, we get

$$(m-1)!\, H(r, r-m) = \begin{vmatrix} (m-1)!\, G(-m-1, r), & \binom{m-1}{1}(r+m)^{(1)}, & \binom{m-1}{2}(r+m)^{(2)}, & \cdots, & (r+m)^{(m-1)} \\ (m-2)!\, G(-m, r), & \binom{m-2}{0}(r+m-1)^{(0)}, & \binom{m-2}{1}(r+m-1)^{(1)}, & \cdots, & (r+m-1)^{(m-2)} \\ (m-3)!\, G(-m+1, r), & 0, & \binom{m-3}{0}(r+m-2)^{(0)}, & \cdots, & (r+m-2)^{(m-3)} \\ \cdots, & \cdots, & \cdots, & \cdots, & \cdots \\ 0!\ G(-2, r), & 0, & 0, & \cdots, & (r+1)^{(0)} \end{vmatrix}$$

where $j^{(l)}$ denotes as usual $j(j-1)(j-2)\cdots(j-l+1)$, we take $j^{(0)} = 1$ and $0^{(0)} = 1$.

---

* As a check on the value of $H(r, r-m)$, notice that $H(r, r-m) = 0$, $r = 1, 2, 3, \cdots m-1$; $m \geqslant 2$.

In view of (2), this determinant can be broken up into m simpler ones. We thus have

$$(m-1)!\ \mathrm{H}(r, r-m) = m^{r+m-1} - \theta_1(r, m)\cdot(m-1)^{r+m-2} + \theta_2(r, m).(m-2)^{r+m-3} - \cdots\cdots + (-1)^{m-1}\theta_{m-1}(r, m) \quad \cdots(7)$$

where $\theta_k(r, m)$ is a determinant of order $(k+1)$.

2. 3. We now proceed to determine the exact form of $\theta_k(r, m)$. We have

$$\theta_k(r, m) =$$

$$\begin{vmatrix} \binom{m-1}{k}(m-k)^k & \binom{m-1}{1}(r+m)^{(1)} & \binom{m-1}{2}(r+m)^{(2)} & \cdots, \binom{m-1}{k}(r+m)^{(k)} \\ -\binom{m-2}{k-1}(m-k)^{k-1} & \binom{m-2}{0}(r+m-1)^{(0)} & \binom{m-2}{1}(r+m-1)^{(1)}, \cdots, & \binom{m-2}{k-1}(r+m-1)^{(k-1)} \\ \binom{m-3}{k-2}(m-k)^{k-2} & 0 & \binom{m-3}{0}(r+m-2)^{(0)}, \cdots, & \binom{m-3}{k-2}(r+m-2)^{(k-2)} \\ \cdots & \cdots & \cdots & \cdots \\ (-1)^k\binom{m-k-1}{0} & 0 & 0 & \cdots, \binom{m-k-1}{0}(r+m-k)^{(0)} \end{vmatrix}$$

Multiplying the rows in order from top to bottom, and dividing the columns in order from left to right by

$$1, \frac{(m-1)^{(1)}}{k^{(1)}}, \frac{(m-1)^{(2)}}{k^{(2)}}, \frac{(m-1)^{(3)}}{k^{(3)}}, \cdots\cdots, \frac{(m-1)^{(k)}}{k^{(k)}};$$

we get

$$\theta_k(r, m) =$$

$$\binom{m-1}{k}\cdot\begin{vmatrix} (m-k)^k & \binom{k}{1}(r+m)^{(1)} & \binom{k}{2}(r+m)^{(2)} & \cdots, (r+m)^{(k)} \\ -(m-k)^{k-1} & \binom{k-1}{0}(r+m-1)^{(0)} & \binom{k-1}{1}(r+m-1)^{(1)}, \cdots, & (r+m-1)^{(k-1)} \\ (m-k)^{k-2} & 0 & \binom{k-2}{0}(r+m-2)^{(0)}, \cdots, & (r+m-2)^{(k-2)} \\ \cdots & \cdots & \cdots & \cdots \\ (-1)^k & 0 & 0 & \cdots, (r+m-k)^{(0)} \end{vmatrix}$$

$$= \binom{m-1}{k}\left\{(m-k)^k + \binom{k}{1}(m-k)^{k-1}(r+m)^{(1)} + \binom{k}{2}(m-k)^{k-2}(r+m)^{(2)} + \cdots + \binom{k}{k}(r+m)^{(k)}\right\} \quad \cdots(8)$$

In Mathematical short-hand, we may write

$$\theta_k(r, m) \overset{b}{=} \binom{m-1}{k}\left\{(m-k) + (r+m)\right\}^k \quad \cdots\cdots(8')$$

$\overset{b}{=}$ indicating that the powers of $(r+m)$ are to be enclosed within brackets.

Since $k \leqslant m-1$, it will be readily seen from (8), that $\theta_k\ (r, m)$ is a polynomial in r of degree k, with positive integral coefficients. This proves Ward's conjecture.

§3. 1. Operations with Δ.

The operator Δ is defined by the relation

$$\Delta\psi\ (n) = \psi\ (n+1) - \psi\ (n).$$

Evidently therefore $\Delta = e^{D} - 1$, where $D = \frac{d}{dn}$.

Also

$$\Delta^j\ (n-j)^s = n^s - \binom{j}{1}(n-1)^s + \binom{j}{2}(n-2)^s - \cdots\cdots + (-1)^j \binom{j}{j}(n-j)^s \quad .. \quad (9)$$

In view of (9), we can write

$$j!\ \mathrm{G}\ (-j-2, r) = \{\Delta^j\ n^{j+r}\}_{n=1}\ ,\quad j \geqslant 0, \quad .. \quad .. \quad (2')$$

and $\quad j!\ \mathrm{G}\ (-j-1, r) = \{\Delta^j\ n^{j+r}\}_{n=0}\ ,\quad j \geqslant 1\ ;$

where $\{\ \}_{n=t}$ indicates that n is to be replaced by t at the end of the operation.

We further have $\quad \Delta^j\ n^{(s)} = s^{(j)} \cdot n^{(s-j)}, \quad .. \quad .. \quad .. \quad (10)$

and

$$\Delta\ \{f_1\ (n) \cdot f_2\ (n)\} = f_1\ (n) \cdot \Delta f_2\ (n) + f_2\ (n+1) \cdot \Delta f_1\ (n) \quad .. \quad (11)$$

3. 2. Action of Δ^s on $\mathrm{G}\ (n, r)$.

We have $\quad \Delta\ \mathrm{G}\ (n, r) = (n+1)\ \mathrm{G}\ (n, r-1) \quad .. \quad .. \quad .. \quad (1')$

Repeated application of (11) gives

$$\Delta^2\ \mathrm{G}\ (n, r) = (n+1)^2\ \mathrm{G}\ (n, r-2) + \mathrm{G}\ (n+1, r-1)\ ;$$

$$\Delta^3\ \mathrm{G}\ (n, r) = (n+1)^3\ \mathrm{G}\ (n, r-3) + (3n+5)\ \mathrm{G}\ (n+1, r-2)\ ;$$

$$\Delta^4\ \mathrm{G}\ (n, r) = (n+1)^4\ \mathrm{G}\ (n, r-4) + (6n^2+20n+17)\mathrm{G}(n+1, r-3) + 3\ \mathrm{G}\ (n+2, r-2)\ ;$$

In general if $\Delta^s\ \mathrm{G}\ (n, r)$

$$= f_0\ (s) \cdot \mathrm{G}\ (n, r-s) + f_1\ (s) \cdot \mathrm{G}\ (n+1, r-s+1) + f_2\ (s) \cdot \mathrm{G}\ (n+2, r-s+2) + \cdots + f_{\left[\frac{s}{2}\right]}(s) \cdot \mathrm{G}\left(n+\left[\frac{s}{2}\right], r-s+\left[\frac{s}{2}\right]\right), \quad .. \quad (12)$$

where the f's are functions of n and s;

then $\Delta^{s+1}\ \mathrm{G}\ (n, r) = (n+1)\ f_0\ (s) \cdot \mathrm{G}\ (n, r-s-1)$

$$+ \sum_{k=1}^{\left[\frac{s}{2}\right]} \{(n+k+1)\ f_k\ (s) + \Delta\ f_{k-1}\ (s)\}\ \mathrm{G}\ (n+k, r-s+k-1) + \Delta\ f_{\left[\frac{s}{2}\right]}(s) \cdot \mathrm{G}\left(n+\left[\frac{s}{2}\right]+1, r-s+\left[\frac{s}{2}\right]\right).$$

Hence

$$f_k(s+1) = (n+k+1) f_k(s) + \Delta f_{k-1}(s), \quad 0 \leqslant k \leqslant \left[\frac{s}{2}\right] + 1; \quad (13)$$

we take

$$f_{-1}(s) = 0, \text{ also } f_t(s) = 0, \text{ if } t > \left[\frac{s}{2}\right].$$

3. 3. We proceed to obtain an elegant expression for $f_k(s)$.

Since $f_0(s) = (n+1) f_0(s-1)$, and $f_0(1) = (n+1)$;

we have $f_0(s) = (n+1)^s$.

Again

$$f_1(s) - (n+2) f_1(s-1) = \Delta f_0(s-1) = (n+2)^{s-1} - (n+1)^{s-1},$$
$$f_1(s-1) - (n+2) f_1(s-2) = \Delta f_0(s-2) = (n+2)^{s-2} - (n+1)^{s-2},$$
$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$
$$f_1(1) - (n+2) f_1(0) = \Delta f_0(0) = (n+2)^0 - (n+1)^0.$$

Multiplying these relations in order by 1, $(n+2)$, $(n+2)^2$, ... and adding, we get without difficulty

$$f_1(s) = \mathrm{D}(n+2)^s - \Delta (n+1)^s,$$
$$= \mathfrak{D} (n+1)^s;$$

where $\mathfrak{D}$ denotes the operator $\mathrm{D}e^{\mathrm{D}} - \Delta$ or $(\mathrm{D}-1)e^{\mathrm{D}} + 1$.

Proceeding as above, we get without much difficulty,

$$2! f_2(s) = \mathfrak{D}^2 (n+1)^s.$$

This suggests the form for $f_k(s)$. We have in fact

$$k! f_k(s) = \mathfrak{D}^k (n+1)^s \quad .. \quad .. \quad .. \quad .. \quad (14)$$

We have simply to show that (14) satisfies (13).

It is well known that

$$\phi(\mathrm{D}) n^{s+1} - n \phi(\mathrm{D}) n^s = \phi'(\mathrm{D}) n^s,$$

where $\phi'(\mathrm{D}) = \dfrac{d}{d\mathrm{D}} \phi(\mathrm{D})$.

It follows that

$$f_k(s+1) - (n+k+1) f_k(s)$$
$$= \frac{1}{k!} \left\{ \mathfrak{D}^k (n+1)^{s+1} - (n+1) \mathfrak{D}^k (n+1)^s - k \mathfrak{D}^k (n+1)^s \right\},$$
$$= \frac{1}{k!} \left\{ \frac{d}{d\mathrm{D}} \mathfrak{D}^k - k \mathfrak{D}^k \right\} (n+1)^s,$$
$$= \frac{1}{(k-1)!} \left\{ \mathrm{D}e^{\mathrm{D}} - \mathfrak{D} \right\} \mathfrak{D}^{k-1} (n+1)^s,$$
$$= \frac{1}{(k-1)!} \Delta \mathfrak{D}^{k-1} (n+1)^s = \Delta f_{k-1}(s).$$

Now, (14) is easily established by inductive reasoning.

Since $\mathcal{D} = (\mathrm{D}-1)\, e^{\mathrm{D}} + 1,$

$$= \frac{\mathrm{D}^2}{2!} + \frac{2\,\mathrm{D}^3}{3!} + \frac{3\,\mathrm{D}^4}{4!} + \cdots + \frac{(j-1)\,\mathrm{D}^j}{j!} + \cdots\cdots$$

so $f_k(s)$ is of degree $s-2k$ in n.

In particular, $f_k(2k) = \frac{(2k)!}{k!\,2^k}$, a constant;

$$f_k(2k+1) = \frac{(2k+1)!}{k!\,2^k \cdot 3}\{3n+3+2k\};$$

and $f_k(s) = 0$ when $k > \left[\frac{s}{2}\right]$.

§4. 1. To prove that for all positive integral values of s,

$$n^s = n^{(s)} + \mathrm{G}(-s, 1)\cdot n^{(s-1)} + \mathrm{G}(-s+1, 2)\cdot n^{(s-2)} + \cdots + \mathrm{G}(-2, s-1)\cdot n^{(1)}.$$

Let $n^s = \sum_{j=1}^{s} c_j\, n^{(j)}$, where the c's are functions of s.

Then, we have $j!\,\mathrm{G}(-j-1, s-j) = \{\Delta^j n^s\}_{n=0}, \qquad j \geqslant 1.$

$$= \left\{\Delta^j \sum_{i=1}^{s} c_i\, n^{(i)}\right\}_{n=0},$$

$$= \left\{\sum_{i=1}^{s} c_i\, (i)^{(j)}\cdot n^{(i-j)}\right\}_{n=0},$$

$$= c_j \cdot j^{(j)} = j!\, c_j.$$

whence $c_j = \mathrm{G}(-j-1, s-j)$,

and $$n^s = \sum_{j=1}^{s} \{\mathrm{G}(-j-1, s-j)\cdot n^{(j)}\}. \qquad \ldots \qquad (15)$$

4. 2. From (15), we readily obtain

$$\sum_{i=1}^{n} i^s = \sum_{j=1}^{s} \left\{\mathrm{G}(-j-1, s-j).\ \frac{(n+1)^{(j+1)}}{j+1}\right\}, \quad s > 0. \quad \ldots \quad (16)$$

Since $(n+1)^{(j+1)} = n^{(j+1)} + (j+1)\, n^{(j)}$,

and $\mathrm{G}(-j, s-j+1) + j\cdot \mathrm{G}(-j-1, s-j) = \mathrm{G}(-j-1, s-j+1)$,

therefore $$\sum_{i=1}^{n} i^s = \sum_{j=1}^{s+1} \left\{\mathrm{G}(-j-1, s-j+1)\cdot \frac{n^{(j)}}{j}\right\}, \quad s \geqslant 1. \quad \ldots \quad (17)$$

In particular, we get

$$\sum_{i=1}^{n} i^3 = \mathrm{G}(-2, 2)\cdot \frac{(n+1)^{(2)}}{2} + \mathrm{G}(-3, 1)\cdot \frac{(n+1)^{(3)}}{3} + \mathrm{G}(-4, 0).\ \frac{(n+1)^{(4)}}{4},$$

$$= \frac{(n+1)^{(2)}}{2} + 3\cdot \frac{(n+1)^{(3)}}{3} + \frac{(n+1)^{(4)}}{4} = \left\{\frac{n(n+1)}{2}\right\}^2.$$

§5. Bernoulli's Numbers.

It is well known that

$$\sum_{i=1}^{n} i^s = \frac{n^{s+1}}{s+1} + \left\{\tfrac{1}{2} + \frac{B_2}{2!} D + \frac{B_4}{4!} D^3 + \frac{B_6}{6!} D^5 + \cdots + \frac{B_{2\left[\frac{s}{2}\right]}}{(2\left[\frac{s}{2}\right])!} D^{2\left[\frac{s}{2}\right]-1}\right\} n^s \quad .. (18)$$

where the B's are Bernoulli's numbers.

Putting $s = 2t$ and equating the coefficients of n in (16), (17) and (18), we get

$$B_{2t} = G(-2, 2t) - \frac{1!}{2} G(-3, 2t-1) + \frac{2!}{3} G(-4, 2t-2) - \cdots + \frac{(2t)!}{2t+1}, \quad .. (19)$$

$$= \frac{0!}{2} G(-2, 2t-1) - \frac{1!}{3} G(-3, 2t-2) + \frac{2!}{4} G(-4, 2t-3) - \cdots - \frac{(2t-1)!}{2t+1} \quad .. (19')$$

Again putting $s = 2t + 1$, we obtain in the same manner,

$$0 = G(-2, 2t+1) - \frac{1!}{2} G(-3, 2t) + \frac{2!}{3} G(-4, 2t-1) - \cdots - \frac{(2t+1)!}{2t+2}, \quad .. (20)$$

$$= \frac{0!}{2} G(-2, 2t) - \frac{1!}{3} G(-3, 2t-1) + \frac{2!}{4} G(-4, 2t-2) - \cdots + \frac{(2t)!}{2t+2} \quad .. (20')$$

These results are easily verified.

§6. To prove that for all positive integral values of $r > 0$,
$G(-2, r) - 1!\, G(-3, r-1) + 2!\, G(-4, r-2) - \cdots + (-1)^r \cdot r!\, G(-r-2, 0) = 0$.
We have $j!\, G(-j-2, r) = \{\Delta^j n^{j+r}\}_{n=1}$.

Now, $\sum_{j=0}^{r} \{(-1)^j \cdot j!\, G(-j-2, r-j)\}$

$= \sum_{j=0}^{r} \{(-1)^j \cdot \Delta^j n^r\}_{n=1}$,

$= \{(1 - \Delta + \Delta^2 - \cdots + (-1)^r \Delta^r)\, n^r\}_{n=1}$,

$= \left\{\frac{1}{1+\Delta} n^r\right\}_{n=1}$; for $\Delta^s n^r = 0$, $s > r$;

$= \{(n-1)^r\}_{n=1} = 0$, since $r \geqslant 1$;

and so the proposition is proved.

REFERENCES.

1. "Sum of Products of first n natural numbers taken r at a time." *Jour. Indian Math. Soc.*, 1931, **19**, 1—6.

2. "Congruence Properties of G-Functions." *Proc. Edinburgh Math. Soc.*, 1934, **4**, 61—66.

"G-Functions in general." *Mathematics Student*, 1935, **3**, 50—55.

3. "Stirlings Numbers and Polynomials." *Amer. Jour. of Math.*, 1934, **56**, 87—95.

4. *Math. Notes*, Edinburgh Math. Soc., 1935, **29**, xi—xiii.

5. *Proc. Ind. Acad. Sci.*, 1935, **1**, 620—622.

POLARISATION OF THE RAMAN BANDS OF WATER AND DEUTERIUM OXIDE.

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(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. *Introduction.*

In two previous communications[1] the author has reported the results of a study of the Raman spectrum of heavy water, and has pointed out the remarkable similarity in the structure and relative intensity of the Raman bands of this substance and those of ordinary water. In order to complete this investigation, it was felt desirable to study the state of polarisation of the Raman bands in the two cases. Results obtained in this direction are communicated in the present paper.

The polarisation of the Raman bands of ordinary water has been studied by Ramaswamy,[2] Cabannes and Rousset,[3] Cabannes and De Riols[4] and Ramakrishna Rao.[5] The results of the different authors are rather conflicting. Ramaswamy found the values 0·6, 0·45 and 0·75 for the depolarisation of the three components of the principal Raman band in the order of increasing frequency. Cabannes and Rousset reported the first component as depolarised and the second one as polarised. Cabannes and De Riols reported quite the contrary result. They found that all the three components are polarised. They gave 0·3 as the depolarisation factor for the central component and remarked that the one of lower frequency is still more polarised. Ramakrishna Rao used a quartz spectrograph in his experiments and got highly anomalous results.

2. *Experimental.*

The liquids (H_2O and D_2O) rendered dust-free by vacuum distillation were contained in suitable Raman tubes of pyrex glass with fused-on end

[1] R. Ananthakrishnan, *Nature*, 1935, **136**, 551.
R. Ananthakrishnan, *Proc. Ind. Acad. Sci.*, (A), 1935, **2**, 291.

[2] C. Ramaswamy, *Nature*, 1931, **127**, 558.

[3] J. Cabannes and A. Rousset, *Ann. de Phys.*, 1933, **19**, 271.

[4] J. Cabannes and J. De Riols, *C. R.*, 1934, **198**, 30.

[5] I. R. Rao, *Z. f. Phys.*, 1935, **90**, 658.

window. The experimental tube was kept at a distance of about 50 cms. from the slit of the spectrograph and light from a 6-inch quartz mercury lamp was concentrated on it by means of a large glass condenser. The observation window was a circular aperture of 3 mms. diameter. A quartz double image prism with its axes horizontal and vertical was interposed between the slit and the Raman tube and fixed in such a position that the two images of the aperture as viewed through the prism could be seen well separated one above the other. A lens behind the double image prism focussed the two images on the slit of the spectrograph (Hilger two-prism glass optical parts). The time of exposure to get an intense picture was about 2 days in the case of water and 4 days in the case of deuterium oxide using a slit width of 75 μ.

3. *Results.*

The spectra photographed in the above manner are reproduced in the plate. The principal results may be summarised as follows:

(1) The three components of the principal Raman bands of H_2O and D_2O are more and more depolarised in the order of increasing frequency shift. The component of lowest frequency shows a high degree of polarisation, the depolarisation factor being probably of the order of 10 or 15%. The component of highest frequency is highly depolarised, perhaps to the limiting value 6/7. The middle component which is the strongest has a depolarisation factor somewhere between these two values, about 40–50%.

(2) The band $\Delta\nu = 1235$ cm.$^{-1}$ in the case of D_2O is depolarised to the extent of 50–60%. The depolarisation of the corresponding Raman band in the case of H_2O ($\Delta\nu = 1650$ cm.$^{-1}$) could not be ascertained because of its unfavourable position in the spectrum. Cabannes and De Riols have found for it the value $\rho \lesssim 0{\cdot}4$.

(3) The band $\Delta\nu = 175$ cm.$^{-1}$ which is quite strong with pronounced anti-stokes is depolarised to the limiting extent of 6/7 in both cases.

(4) The diffuse bands $\Delta\nu = 500$ cm.$^{-1}$ and $\Delta\nu = 750$ cm.$^{-1}$ in the case of H_2O seem to be highly depolarised. The corresponding Raman bands $\Delta\nu = 350$ cm.$^{-1}$ and $\Delta\nu \lesssim 500$ cm.$^{-1}$ recently reported by Magat[6] in the case of D_2O are hardly perceptible in the author's photographs.

4. *Discussion of Results.*

A strict and satisfactory interpretation of the Raman spectra of liquid H_2O and D_2O appears to be very difficult indeed. Nevertheless, there have been certain attempts in this direction, although only of an empirical nature.

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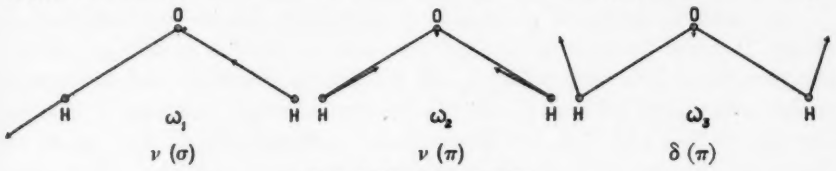
[6] M. Magat, *C. R.*, 1935, **201**, 668.

Mecke's analysis of the vibration-rotation spectrum of ordinary water vapour led him to the choice of the following normal frequencies for the H_2O



Normal Vibrations of H_2O.

molecule in the vapour state. $\nu(\sigma) = \omega_1 = 3795$ cm.$^{-1}$; $\nu(\pi) = \omega_2 = 3670$ cm.$^{-1}$; $\delta(\pi) = \omega_3 = 1615$ cm.$^{-1}$ These may be compared with the infra-red absorption maxima at 3756 and 1595 and the Raman line at 3654 cm.$^{-1}$ observed in the Raman spectrum of water vapour.

The infra-red absorption spectra of liquid H_2O and D_2O have been studied recently by Ellis and Sorge.[7] They have identified the absorption maxima at 6·2 μ (1613 cm.$^{-1}$) and 3 μ (3330 cm.$^{-1}$) in the case of liquid water with the fundamental frequencies assigned by Mecke to the H_2O molecule. The shift in the absorption maxima from the gaseous state to the liquid state is not surprising when it is remembered that many of the molecules contributing to these bands are parts of polymer molecules. Ellis and Sorge have also pointed out that more detailed information about the 3 μ absorption region is to be sought for from the Raman spectrum which yields three components, the average of the maxima being approximately 3220, 3430, and 3600 cm.$^{-1}$ The effect of temperature on the 3 μ Raman band of water is to diminish the intensity of the component of lowest frequency and increase the intensity of the component with the highest frequency. This is explained as being due to breaking up of the polymerised molecules. Ellis and Sorge have therefore chosen the Raman bands at 3430 and 3600 to correspond to the vibrational modes $\nu(\pi)$ and $\nu(\sigma)$ respectively *for the H_2O molecules in the liquid state.* Magat[8] on the other hand has suggested that in so far as the component of frequency 3600 is extremely weak if not entirely absent at low temperatures and increases in intensity as the temperature is raised, it should be identified with the Raman line 3654 of water vapour and arises from a small percentage of water molecules which possess free rotation. The two other components 3220 and 3430 which are quite intense at ordinary temperature represent according to him the fundamental frequencies $\nu(\pi)$ and $\nu(\sigma)$ of the liquid molecules. Ramakrishna Rao's suggestion that the

[7] J. W. Ellis and B. W. Sorge, *Jour. Chem. Phys.*, 1934, **2**, 559.

[8] M. Magat, *Bull. de la Soc. de Phys.*, 1935, **60**, 65.
M. Magat, *C.R.*, 1935, **201**, 669.

component bands at 3220, 3430, and 3600 ought to be attributed respectively to the molecules $(H_2O)_3$, $(H_2O)_2$, and H_2O is only conjectural.

In order to interpret at least in a qualitative fashion the polarisation results, it might be pointed out that the polarisation rules in Raman scattering give the depolarisation factor 6/7 for anti-symmetrical and degenerate modes, and values between 0 and 6/7 for symmetrical vibrations. Thus in the case of H_2O and D_2O, the Raman band corresponding to $\nu\,(\sigma)$ would be highly depolarised, while those corresponding to $\nu\,(\pi)$ and $\delta\,(\pi)$ would show a lesser degree of depolarisation. It is also reasonable to conclude that $\delta\,(\pi)$ would be much more depolarised than $\nu\,(\pi)$.

The high depolarisation of the Raman band at 3600 renders it difficult to identify it with the vapour frequency 3654 which presumably corresponds to $\nu(\pi)$. Rather, it supports the view of Ellis and Sorge that it arises from the anti-symmetrical vibration of the liquid molecules. The high degree of polarisation of the component band at 3220 on the other hand suggests that it should arise from a symmetrical vibration.

It appears that the influence of temperature as well as the observed polarisation results could be satisfactorily explained if we postulate that the liquid state is composed of a large percentage of polymerised molecules (di-hydrol) and a smaller percentage of non-polymerised molecules. To the former belong the vibrational frequencies. $\nu\,(\pi) = 3220$ and $\nu\,(\sigma) = 3430$ while to the latter belong the frequencies $\nu\,(\pi) = 3430$ and $\nu\,(\sigma) = 3600$. This assumption will naturally explain the intermediate degree of depolarisation observed for the central component since it is now a superposition of the depolarised anti-symmetrical vibration of the polymerised and the symmetrical vibration of the non-polymerised molecules. The observation of Magat that the intensity maximum displaces itself in the direction of increasing frequency in the two stronger components as the temperature is raised is also not difficult to understand on this assumption since the coupling between two molecules is bound to be influenced by forces of thermal agitation.

If the view suggested above is correct, the same considerations should explain the Raman spectrum of heavy water as well. The vibrational frequencies of the liquid D_2O molecules appear in the Raman spectrum as a sharp band at 1235 cm.$^{-1}$ and a broad and intense band at 2500 cm.$^{-1}$ The latter band shows a structure exactly analogous to the corresponding Raman band of ordinary water, with two strong components at 2360 and 2510 and a fainter one at 2660. Polarisation photographs show quite analogous features.

Polarisation of Raman Bands.

(i) D_2O (ii) H_2O

The infra-red spectrum of the liquid investigated by Ellis and Sorge led them to the choice of the absorption bands at $8 \cdot 2\,\mu$ (1220 cm.$^{-1}$) and $4\,\mu$ (2500 cm.$^{-1}$) as corresponding to the fundamental frequencies. The fundamental vapour frequencies in the infra-red observed by Barker and Sleator[9] and by Bartholomé and Clusius[10] are 2775 and 1185, while Rank, Larsen and Bordner[11] found a single Raman line at 2666 cm.$^{-1}$ for the vapour which presumably arises from the symmetric vibration.

The origin of the strong low frequency Raman band at 175 cm.$^{-1}$ has been diversely interpreted. The strong infra-red absorption in practically the same region as well as the high depolarisation exhibited by this Raman band, would seem to favour the view that it arises from the hindered rotation or angular oscillation of the liquid molecules. Magat's suggestion[12] that this band owes its origin to the mutual oscillation of the centres of gravity of two liquid molecules without change of orientation cannot explain the high depolarisation observed for this band.

In conclusion, the author wishes to record his respectful thanks to Professor Sir C. V. Raman for his kind interest and guidance in the present work.

5. *Summary.*

The Raman spectra of liquid H_2O and D_2O have been photographed by interposing a double image prism in front of the slit of the spectrograph. The three components of the principal Raman band in the two cases are more and more depolarised in the order of increasing frequency, the component of lowest frequency being highly polarised, and that of highest frequency being highly depolarised. The band $\Delta\nu = 1235$ cm.$^{-1}$ in the case of D_2O is imperfectly polarised, while the low frequency Raman band($\Delta\nu \backsimeq 175$ cm.$^{-1}$) is depolarised to the extent of 6/7 in both cases. A tentative explanation is suggested to interpret the observed results.

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[9] E. F. Barker and W. W. Sleator, *Jour. Chem. Phys.*, 1935, **3**, 660.

[10] E. Bartholomé and K. Clusius, *Naturwiss.*, 1934, **22**, 40; *Z. f. Elek. Chem.*, 1934, **40**, 530.

[11] D. H. Rank, K. D. Larsen and E. R. Bordner, *Jour. Chem. Phys.*, 1934, **2**, 464.

[12] M. Magat, *loc. cit.*

ANTISEPTICS AND ANTHELMINTHICS.

Part II. A Synthesis of 6-Benzyl-7-hydroxyflavone and 6-*n*-Hexyl-7-hydroxyflavone.

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and
K. Venkataraman.
(From the Forman Christian College, Lahore, and the Department of Chemical Technology, the University, Bombay.)

Received February 10, 1936.

In view of the therapeutic value of hexylresorcinol[1] as an internal antiseptic[2] extensive work on the alkyl derivatives of other phenols has been reported.[3]

Since the anthelminthic constituent of the leaves of *Calycopteris floribunda* has been identified as a dihydroxytetramethoxyflavone[4] the examination of Indian plants with alleged vermicidal action for the presence of flavone derivatives, and of synthetic specimens of the latter for anthelminthic properties, has become relevant to the general attempt to prepare new antiseptics and anthelminthics.[5] Nakao and Tseng[6] have isolated apigenin and its 7-methyl ether from the Chinese drug "Yuen-hua", believed from very early times to be a diuretic and anthelminthic, but the pharmacological action has not been correlated with the flavone content. The present work relates to the synthesis of the 6-benzyl and hexyl derivatives of 7-hydroxyflavone. The influence of a C-benzyl group on the bactericidal action of phenols and halogenated phenols has been demonstrated by Klarmann, Gates and Shternov.[7]

4-Benzylresorcinol (2 : 4-dihydroxydiphenylmethane) was prepared according to Klarmann[8]; the homogeneity of the product and the absence of

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[1] Johnson and Lane, *J. Amer. Chem. Soc.*, 1921, **43**, 348.

[2] Leonard and others, *J. Amer. Med. Assoc.*, 1924, **83**, 2005, *et sequa.*

[3] Dohme, Cox and Miller, *J. Amer. Chem. Soc.*, 1926, **48**, 1688; Klarmann and Wowern, *J. Amer. Chem. Soc.*, 1929, **51**, 605; Brewster and Harris, *J. Amer. Chem. Soc.*, 1930, **52**, 4866; Coulthard, Marshall and Pyman, *J. Chem. Soc.*, 1930, **137**, 280; Klarmann, *Soap*, 1932, **8**, 99; 1934, **10**, 87; etc.

[4] Ratnagiriswaran, Sehra and Venkataraman, *Biochem. Jour.*, 1934, **28**, 1964.

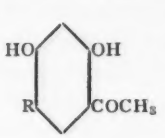
[5] Gulati, Seth and Venkataraman, *Jour. pr. Chem.*, 1933, **137**, 47.

[6] *Jour. Pharm. Soc. Japan*, 1932, No. **602**, 343; 1933, No. **608**, 905.

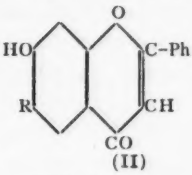
[7] *J. Amer. Chem. Soc.*, 1932, **54**, 3315.

[8] *J. Amer. Chem. Soc.*, 1926, **48**, 791.

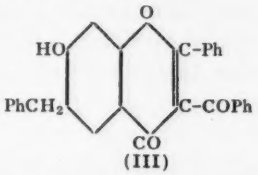
2 : 4-dibenzylresorcinol were confirmed by comparison with the product of the Clemmensen reduction of resobenzophenone. The phenol was then converted into 5-benzylresacetophenone (I ; R = CH_2Ph) by a Hœsch reaction with acetonitrile. Treatment of the ketone with benzoic anhydride led to a mixture of 6-benzyl-7-hydroxyflavone (II ; R = CH_2Ph) and



(I)

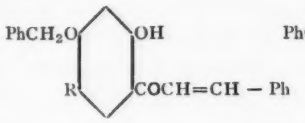


(II)

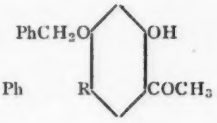


(III)

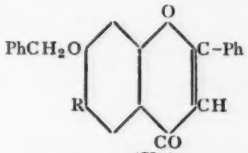
its 3-benzoyl derivative (III), the former being also prepared by the selenium dioxide oxidation of the chalkone (IV ; R = CH_2Ph), followed by debenzylation.



(IV)



(V)



(VI)

By analogy with the Fries reaction on 7-acyloxycoumarins and chromones,[9] which give rise to 8-substituted products, the Claisen change of 7-benzyloxyflavone was studied with the object of preparing 7-hydroxy-8-benzylflavone, but attempts at migration with zinc chloride or aluminium chloride resulted only in unchanged material or debenzylation to 7-hydroxyflavone. Difficulties were also encountered in efforts to prepare 7-hydroxy-8-benzoylflavone and reduce it to the desired substance.

By submitting 4-*n*-hexylresorcinol to the series of reactions outlined in the case of 4-benzylresorcinol, the ketone (I ; R = *n*-hexyl), the chalkone (IV ; R = *n*-hexyl) and the flavone (II ; R = *n*-hexyl) were prepared.

Experimental.

C-Benzylresorcinol.—(*a*) Prepared according to Klarmann (*loc. cit.*) the substance was obtained in a yield of 35%, the oil distilling at 198–200°/2 mms. The colourless needles from petroleum ether melted at 76–77°. (*b*) A mixture of resorcinol (25 g.), benzyl chloride (7·5 g.) and fused zinc chloride (2 g.) was warmed carefully on the water-bath until a vigorous reaction set in. More benzyl chloride (7·5 g.) was then added, the whole being finally heated for one hour on the water-bath. On cooling, water was added, the mixture

[9] Limaye, *Ber.*, 1934, **67**, 12; Wittig, Baugert and Richter, *Ann.*, 1925, **446**, 184.

extracted with ether, the ether extract washed with 2% sodium carbonate solution, dried and the solvent removed. Distillation of the residue *in vacuo* gave 15 g. of an oil boiling at 210-220°/12-13 mms., which was redistilled and collected at 198-200°/2 mms. (8 g.). (*c*) Resobenzophenone (20 g.), zinc amalgam (86 g.), aldehyde-free alcohol (60 g.) and 50% hydrochloric acid (140 g.) were boiled for 30 hours, when a drop of the oily product, taken up in alcohol and carefully neutralised, gave no colouration with ferric chloride. Ether extraction and distillation at 2 mms. pressure gave C-benzylresorcinol in 50% yield.

C-Benzylresacetophenone (I ; R = CH_2Ph).—After saturation of a mixture of C-benzylresorcinol (10 g.), acetonitrile (3·5 c.c.), ether (30 c.c.) and zinc chloride (4 g.) with hydrogen chloride, and 4 days in the ice-chest, the ether was decanted off, the residue boiled with water (250 c.c.) and filtered hot. The undissolved oil solidified on cooling and crystallised from benzene in very pale yellow leaflets (6 g.), m.p. 153° (Found : C, 74·1 ; H, 5·7. $C_{15}H_{14}O_3$ requires C, 74·4 ; H, 5·8%). The alcoholic solution exhibited a deep violet colouration with ferric chloride. The *dinitrophenylhydrazone* melted at 221° (Found : N, 13·0. $C_{21}H_{18}O_6N_4$ requires N, 13·3%). When the reaction was carried out with an impure C-benzylresorcinol, b.p. 210-220°/10-12 mms., the hot aqueous filtrate after removal of C-benzylresacetophenone, deposited colourless leaflets (0·4 g.) on cooling, which melted at 209° and gave an orange-red ferric chloride colouration (Found : C, 75·0 ; H, 5·9).

2-*Hydroxy*-4-*benzyloxy*-5-*benzylacetophenone* (V ; R = CH_2Ph).—Benzylation in the known manner[10] gave the ether, which crystallised from alcohol in colourless needles, m.p. 111° (Found : C, 79·4 ; H, 6·0. $C_{22}H_{20}O_3$ requires C, 79·5 ; H, 6·0%). The colour with ferric chloride was deep red.

2-*Hydroxy*-4-*benzyloxy*-5-*benzylchalkone* (IV ; R = CH_2Ph).—To a warm solution of the above ketone (2·3 g.) and benzaldehyde (1·3 g.), 50% caustic soda solution (6 g.) was added. On leaving overnight, the chalkone was isolated as usual. The deep yellow needles (2·3 g.) from glacial acetic acid melted at 134° (Found : C, 82·8 ; H, 6·2. $C_{29}H_{24}O_3$ requires C, 82·9 ; H, 5·7%). The crystals were coloured orange-red by sulphuric acid.

6-*Benzyl*-7-*benzyloxyflavone* (VI ; R = CH_2Ph).—From a mixture of the above chalkone (2 g.), selenium dioxide (2 g.) and amyl alcohol (12 c.c.), refluxed at 150° for 12 hours, the solvent was removed in steam, and the residue extracted with glacial acetic acid. The colourless needles (1 g.) separating from the filtrate melted at 222° (Found : C, 83·0 ; H, 5·4.

[10] Gulati, Seth and Venkataraman, *J. Chem. Soc.*, 1934, 1766.

$C_{29}H_{22}O_3$ requires C, 83·2 ; H, 5·3%). The colourless solution in sulphuric acid exhibited a blue fluorescence.

6-*Benzyl*-7-*hydroxyflavone* (II ; R = CH_2Ph).—To the benzyl ether (1 g.) in glacial acetic acid (10 c.c.), hydrobromic acid saturated at 0° (10 g.) was added and the solution refluxed for an hour. Dilution with water and crystallisation of the precipitate from glacial acetic acid gave cream-coloured, elongated, triangular plates, m.p. 267° (Found : C, 80·6 ; H, 5·0. $C_{22}H_{16}O_3$ requires C, 80·5 ; H, 4·9%). The *acetyl* derivative, colourless needles from alcohol, melted at 191° (Found : C, 78·1 ; H, 4·9. $C_{24}H_{18}O_4$ requires C, 77·8 ; H, 4·8%).

3-*Benzoyl*-6-*benzyl*-7-*hydroxyflavone* (III).—The Robinson reaction with C-benzylresacetophenone (4 g.), benzoic anhydride (40 g.) and sodium benzoate (8 g.), hydrolysis with 10% alcoholic potash (240 c.c.) and saturation with carbon dioxide led to a yellow powder, crystallisation of which from glacial acetic acid gave colourless plates (1·5 g.), m.p. 267°, identical with the previously obtained flavone. Concentration of the mother-liquors and dilution gave thin, colourless plates, m.p. 229° (Found : C, 80·2 ; H, 4·6. $C_{29}H_{20}O_4$ requires C, 80·6 ; H, 4·6%).

C-Hexylresacetophenone (I ; R = *n*-hexyl).—The product, obtained by the Hoesch reaction between hexylresorcinol[11] (30 g.) acetonitrile (12 g.) and zinc chloride (12 g.) in ether (50 c.c.), followed by aqueous hydrolysis, was an oil, which was taken up in ether. After removal of the ether from the dried extract and distillation of the residue *in vacuo*, the fraction coming over at 195-200°/3-4 mms. solidified in contact with light petroleum. The colourless plates (24 g.) from the same solvent melted at 85° (Found : C, 71·1 ; H, 8·7. $C_{14}H_{20}O_3$ requires C, 71·2 ; H, 8·5%). The ferric chloride colouration was deep red. The *dinitrophenylhydrazone* melted at 183-184° (Found : N, 13·3. $C_{20}H_{24}O_6N_4$ requires N, 13·4%).

2-*Hydroxy*-4-*benzyloxy*-5-*hexylacetophenone* (V ; R = *n*-hexyl).—The colourless needles from alcohol melted at 94° (Found : C, 77·6 ; H, 8·2. $C_{21}H_{26}O_3$ requires C, 77·3, H, 8·0%).

2-*Hydroxy*-4-*benzyloxy*-5-*hexylchalkone* (IV ; R = *n*-hexyl).—Yellow needles from alcohol, m.p. 92° (Found : C, 81·3 ; H, 7·4. $C_{28}H_{30}O_3$ requires C, 81·1 ; H, 7·2%). The alcoholic solution turned dark brown with ferric chloride.

6-*Hexyl*-7-*benzyloxyflavone* (VI ; R = *n*-hexyl).—The oxidation of the chalkone (16 g.) with selenium dioxide (18 g.) resulted in an oil, which

[11] Dohme, Cox and Miller, *Jour. Amer. Chem. Soc.*, 1926, **48**, 1688.

solidified on cooling, and the colourless needles (4 g.) from glacial acetic acid melted at 120° (Found : C, 81·5 ; H, 6·9. $C_{28}H_{28}O_3$ requires C, 81·5 ; H, 6·7%).

6-Hexyl-7-hydroxyflavone (II ; R = *n*-hexyl).—Colourless needles from alcohol, m.p. 191–192° (Found: C, 78·5 ; H, 6·9. $C_{21}H_{22}O_3$ requires C, 78·3 ; H, 6·8%). The alcoholic solution was unchanged in colour by the addition of ferric chloride and the colourless solution in sulphuric acid showed a blue fluorescence. The *acetyl* derivative, colourless needles from alcohol, melted at 104° (Found : C, 75·5 ; H, 6·6. $C_{23}H_{24}O_4$ requires C, 75·8 ; H, 6·6%).

SCATTERING OF LIGHT IN OPTICAL GLASSES.

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Received February 3, 1936.

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction.

The constitution and structure of glass have long been a puzzling problem. It is, nevertheless, true to say that there has been comparatively little work done of a fundamental or theoretical nature. This is no doubt due to the meagre knowledge we possess concerning the constitution of glass. It is obvious that glasses do not consist of crystallites which can be recognised as such by the naked eye even when assisted by powerful microscopes. Glasses are usually described as supercooled liquid or as an amorphous solid ; the word amorphous as used by the workers on glass is taken to mean that no crystallites can be detected by the ordinary laboratory methods. From its state of aggregation one is led to believe that glass is a supercooled liquid for it exhibits a series of thermodynamic characteristics of such a condition. Data on specific heat, surface tension, melting point, viscosity and dielectric strength indicate that the material is of high molecular weight or highly associated. But on the other hand as regards its elastic properties, glass behaves more or less like a hard rigid solid.

X-ray diffraction by glasses has been studied in detail by numerous investigators beginning with Debye and Scherrer. The lack of obvious crystallinity makes it clear that sharp diffraction patterns are unlikely to be obtained. Most glasses exhibit broad and diffuse bands similar to those obtained in the case of ordinary liquids. Randall and Rooksby[1] tried to explain the different bands on the basis of minute crystals or groups of atoms regularly arranged over a very small volume. But such a view regarding the constitution of glass does not find support from other directions.

It has long ago been pointed by Prof. Raman[2] that a study of the scattering of light in glasses would enhance our knowledge regarding the nature of glass and amorphous substances in general, to a considerable extent. The present

[1] J. T. Randall and H. P. Rooksby, *Journ. Soc. Glas. Techn.*, 1933, **17**, 287.

[2] C. V. Raman, *Molecular Diffraction of Light*, 1922.

Lord Rayleigh[3] was the first to demonstrate the existence of an internal scattering of light in common glasses. The degree of depolarisation was found to be of the same order of magnitude as that usually observed in gases. He was inclined to attribute the scattering in glasses to spherical inclusions of diameter not small compared with the wavelength of light and explained the finite depolarisation of the scattered light as due to the appreciable size of these inclusions. It is well known that opal glasses owe their diffusing properties to the fact that they contain in suspension small crystals which can be observed under an ordinary microscope, of refractive index and absorption coefficient different from those of the glassy matrix. But it is hard to believe that such inclusions may also exist in optical glasses. Prof. Raman[4] has reported the measurements of intensity and depolarisation of light scattered by a series of optical glasses. The closest examination by him under a powerful microscope with dark ground illumination failed to indicate the presence of any visible inclusions. Consequently he came to the conclusion that the scattering in these glasses was really molecular in origin. He found that the scattering power of glass approximated to that of a liquid and not to that of a crystal.

The observations of the above-mentioned investigators on the scattering of light in glass did not carry us far into the more intricate problem concerning the constitution of glass, for they studied the Rayleigh radiation with incident unpolarised light alone. In order to get more comprehensive and fundamental information regarding the state of aggregation or dispersion of molecules in any scattering medium, it is essential to make a comparative study of the state of polarisation of the scattered light with the incident light in different states of polarisation, (namely, unpolarised, vertically polarised and horizontally polarised). This fact has often been stressed by the author in recent papers[5] in these *Proceedings*. If glass is an aggregate of molecular clusters, the light scattered transversely when the incident light is polarised with electric vector horizontal, will no longer be completely unpolarised as in the case of an ordinary liquid or gas but will be partially polarised with the horizontal component stronger than the vertical component to an extent depending upon the size of the clusters present. The object of the present investigation is to make a more detailed study of the scattering of light in a series of optical glasses of widely different composition and to discuss the bearing of the results on the constitution of glass.

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[3] R. W. Strutt, (Lord Rayleigh), *Proc. Roy. Soc.*, 1919, **95**, 476.

[4] C. V. Raman, *Journ. Optical Soc. America*, 1927, **15**, 185.

[5] R. S. Krishnan, *Proc. Ind. Acad. Sci.*, 1934-5, **1**, 211; 717; 782; 915. 1935, **2**, 221.

2. *Specimens Examined.*

TABLE I.

Serial No.	Melting No.	Glass contains traces of Al_2O_3, Fe_2O_3, As_2O_3 and oxides in:		Density
		more than 10%	less than 10%	
1	25188	SiO_2, B_2O_3, Al_2O_3, K_2O	Na_2O, F	2·3
2	18415	SiO_2, B_2O_3, K_2O	Al_2O_3	2·3
3	16776	SiO_2, K_2O	Al_2O_3, Na_2O, CaO	2·4
4	23975	SiO_2, B_2O_3, ZnO	Al_2O_3, Na_2O	2·5
5	24906	SiO_2, B_2O_3	Na_2O, K_2O, BaO	2·5
6	22601	SiO_2, B_2O_3, Sb_2O_3	Al_2O_3, Na_2O, K_2O	2·7
7	23125	SiO_2, Na_2O, PbO	ZnO	2·7
8	22638	SiO_2, PbO	Na_2O, K_2O	2·9
9	24464	SiO_2, ZnO, BaO	B_2O_3, Na_2O, K_2O, PbO	3·1
10	19510	SiO_2, PbO	Na_2O, K_2O	3·2
11	23355	SiO_2, B_2O_3, BaO	Al_2O_3, Na_2O	3·3
12	20672	SiO_2, PbO	B_2O_3, Na_2O, K_2O	3·4
13	22986	SiO_2, BaO, PbO	Na_2O, K_2O, ZnO	3·5
14	23441	SiO_2, PbO	Na_2O, K_2O	3·9
15	23497	SiO_2, BaO, PbO	Na_2O, K_2O, ZnO	3·9
16	23850	SiO_2, PbO	Na_2O, K_2O	4·4
17	23590	SiO_2, PbO	Na_2O, K_2O	5·1

Table I gives the list of seventeen optical glasses and also their composition and density as furnished by the manufacturers. These glasses were manufactured and were presented to Prof. C. V. Raman by Messrs. Schott and Gen. in Jena (Germany). They are in the form of rectangular slabs (3 cm., 3 cm., 2 cm.) with all the faces excluding the two end faces well polished. The list comprises a representative collection of optical glasses of widely different densities and composition.

3. *Preliminary Observations.*

The specimen to be examined was kept immersed in dust-free distilled water contained in a rectangular cell. The cell was suitably blackened on the outside excepting for three windows. A narrow beam of sunlight reflected by a single mirror Foucault Heliostat was focussed by means of a

long focus lens. At the focus the light passed through the specimen. The track inside the glass was intensely coloured blue when viewed in the transverse direction. It was of uniform colour and intensity throughout. When the track inside the specimen was viewed in the direction of the incident beam with the aid of a microscope no visible speck was observed, the track being throughout homogeneous.

On examining the light scattered transversely with a double-image prism, the two components observed were very different in colour and intensity, showing thereby that the scattered light was strongly but not completely polarised. The vertical component which was very much more intense was a rich blue in colour. The difference in colour is indicative of a weak fluorescence. Suitable colour filters were introduced in the path of the incident beam to exclude fluorescence. It was found that with an orange filter in the path of the incident beam, the two components of the scattered light were identical in colour for all the specimens.

Table II gives the colours of the vertical and horizontal components of the light scattered transversely by the different optical glasses when a narrow beam of unpolarised white light is passed through them. The refractive index of each specimen for the yellow line of sodium was measured with the aid of a Pulfrich Refractometer.

4. Measurement of Depolarisation.

The light from a 25 ampere projection lantern was condensed on a small square aperture (of edge 2 mm.). A long focus lens (aperture=4 cm.) served to condense the light emerging out of the aperture on to the glass to be examined which was placed at a distance of about 50 cm. from the lens. A double-image prism was placed in the path of the incident beam by the side of the lens. The scattered light was viewed through another double-image prism. It was found that the fourth image which was the horizontal component of the scattered light arising from the horizontal component of the incident beam was found to be distinctly brighter than either of the middle two equal anisotropic components. This indicated at once that the optical heterogeneity of the glassy medium should no longer be identified as due to the individual molecules, but due to small groups of molecules. Using incident unpolarised light, light polarised with electric vector, vertical and horizontal respectively, the three depolarisation factors ρ_u, ρ_v and ρ_h of the scattered light corresponding to the three cases were measured using a double-image prism and a nicol, with the orange filter in the path of the incident beam. ρ_u and ρ_v are defined as the ratio of the horizontal component to the vertical component, while ρ_h is defined as the ratio of the vertical component to the horizontal component.

TABLE II.

S. No. as in Table I	Density	Refractive Index μ_D	With incident unpolarised white light		
			Colour of the transversely scattered light	Colour of the vertical component of the same	Colour of the horizontal component of the same
1	2·3	1·4670	Bluish green	Greenish blue	Yellowish green
2	2·3	1·4925	Bluish white	Blue	Greenish yellow
3	2·4	1·5022	Greenish blue	Blue	Greenish yellow
4	2·5	1·5095	Deep blue	Deep blue	Yellowish brown
5	2·5	1·5269	Green	Bluish green	Yellowish green
6	2·7	1·5294	Blue	Blue	Brown
7	2·7	1·5370	Blue	Blue	Green
8	2·9	1·5449	Blue	Blue	Green
9	3·1	1·5697	Blue	Blue	Yellowish brown
10	3·2	1·5698	Blue	Blue	Greenish yellow
11	3·3	1·5892	Blue	Blue	Yellowish green
12	3·4	1·5983	Blue	Blue	Orange
13	3·5	1·6163	Blue	Blue	Yellowish brown
14	3·9	1·6473	Blue	Blue	Indigo-blue with a pink tinge
15	3·9	1·6498	Blue	Bluish white	Indigo-blue with a pink tinge
16	4·4	1·7130	Blue	Blue	Indigo-blue with a pink tinge
17	5·1	1·7850	Greenish blue	Greenish blue	Greenish yellow

The errors arising from the finite angle of convergence of the incident beam were calculated using Ananthakrishnan's formulæ.[6] The actual angle of convergence of the beam inside the specimen was equal to $4/50 \times 2/3$ radian. For this particular angle of convergence the corrections for ρ_u and ρ_v were 0·00035 and 0·00017 respectively. Since the observed values of ρ_u and ρ_v were of the order of 0·03 to 0·01 the correction factors could be neglected. In the same way the correction for ρ_h could also be neglected in comparison with the observed value of ρ_h. The values of ρ_u, ρ_v and ρ_h for the glasses examined are given in Table III.

[6] R. Ananthakrishnan, *Proc. Ind. Acad. Sci.*, 1935, 2, 133.

5. Intensity Measurements.

For the measurement of the relative intensity of scattering in these glasses, the photo-electric method was employed. The method consists in allowing the scattered light to fall on a photo-cell which was connected to a direct current valve bridge amplifier. For very weak intensities the deflections of the galvanometer in the amplifier circuit was a direct measure of the intensity of light falling on the photo-cell. Relatively low scattering power in these glasses especially with an orange filter in the path of the incident beam necessitated recourse to sunlight. A parallel beam of sunlight reflected by a single mirror Foucault Heliostat was condensed by means of a long focus photographic lens provided with an iris diaphragm. At the focus the light passed through the specimen of optical glass contained in the cell of water.

TABLE III.

S. No. as in Table I	Refractive index μ_D	With orange filter in the path of the incident beam					
		ρ_v %	ρ_u %	ρ_h (observed) %	ρ_h (calculated) %	$\Delta\rho_u = \rho_u - \frac{2\rho_v}{1+\rho_v}$	Intensity relative to ether = 1
1	1·4670	12·7	26	78	77	3·5	0·8
2	1·4925	12	24	82	81	2·6	1·0
3	1·5022	3·5	8·1	72	72	1·3	1·9
4	1·5095	0.46	1·2	68	62	0·3	3·3
5	1·5269	3·6	8·1	80	75	1·05	0·9
6	1·5294	3·5	7·5	85	82	0·7	1·2
7	1·5370	2·4	5·2	78	82	0·5	2·1
8	1·5449	3·0	6·1	91	91	0·3	2·1
9	1·5697	2·1	4·8	81	75	0·7	1·8
10	1·5698	3·3	7·0	88	84	0·6	1·3
11	1·5892	2·1	4·6	80	82	0·5	1·6
12	1·5983	3·3	7·0	83	84	0·6	1·6
13	1·6163	1·6	3·7	80	74	0·5	2·4
14	1·6473	2·3	5·2	75	76	0·7	..
15	1·6478	2·0	4·5	77	77	0·6	1·9
16	1·7130	2·5	5·3	87	85	0·4	1·8
17	1·7850	2·8	5·9	87	86	0·5	2·2

The whole arrangement was set up inside a dark cabin. The photo-cell was enclosed in a suitable box and was placed in front of the specimen in such a way that when the screen in front of the photo-cell was raised, only the light scattered by the specimen in the exact transverse horizontal direction entered the photo-cell. One of the glasses was kept as the standard for comparison of intensities of scattering. With the orange filter in the path of the incident beam,the glasses were placed inside the cell of water at the focus of the incident beam one after another in quick succession and the corresponding deflections of the galvanometer in the amplifier circuit were recorded. In order to avoid errors arising from the variations in intensity of the incident beam, the readings with the standard glass were taken before and after each one of the glasses was examined. Finally the scattering power of the standard glass was compared with that of pure dust-free ether contained in a double bulb. From the galvanometer deflections the scattering power of each specimen was calculated in terms of that of ether. The values are given in Table III.

6. *Discussion of Results.*

The sixth column in Table III gives the values of ρ_h calculated from the observed values of ρ_u and ρ_v applying the general Reciprocity Relation

$$\rho_u = (1 + {}^1/\rho_h) / (1 + {}^1/\rho_v) \quad .. \qquad .. \qquad .. \quad (1)$$

The agreement between the calculated and the observed values of ρ_h is quite satisfactory.

Almost all the glasses examined are fluorescent. But this fluorescence is rather weak unlike that in ordinary viscous liquids. The colour of the fainter component is found to be largely influenced by this fluorescence and consequently it varies from glass to glass. On spectroscopic examination it is found that this weak fluorescence is mainly due to a Raman effect together with a faint continuous fluorescence band superposed on it. This continuous band which extends over several hundred Angstrom units is found to change its position for different specimens.

The light scattered by these glasses is strongly polarised as is seen from the low value of ρ_u. The rather high value of ρ_u for glasses 1 and 2 may be due to the higher anisotropy of the scattering elements in them. It is to be noted that for all the glasses, the value of ρ_h is definitely less than 100%. This furnishes us for the first time positive evidence for the existence of molecular aggregates in glass, the size of which is not excessively small compared with the wavelength of light. The depolarisation ρ_u arises not only from the anisotropy of the scattering elements but also from their finite size. To a first approximation the anisotropic part of ρ_u can be considered

to be equal to $2\rho_v/(1+\rho_v)$. The difference $\Delta\rho_u$ between the observed value of ρ_u and $2\rho_v/(1+\rho_v)$ represents the depolarisation due to finite size. Values of $\Delta\rho_u$ are given in Table III. $\Delta\rho_v$ is of the order of 0·6%. That this value of $\Delta\rho_u$ is definite but small indicates that the molecular aggregates are not of large size.

Coming to the intensity of scattering, it is seen that the scattering power of glass is of the same order of magnitude as that of an ordinary liquid or liquid mixture, and not as that of an ordinary crystal. A close scrutiny of the figures in Table III reveals the fact that glasses which possess high scattering power give low depolarisation values. Of all the glasses examined the intensity of scattering is maximum for the glass marked 4. The values of ρ_u, ρ_v and ρ_h for this glass are 1·2%, 0·46% and 62%. They are the lowest observed. It can be inferred from this that in addition to the density scattering and orientation scattering, there may exist composition scattering also in glasses as in the case of liquid mixtures. The transverse scattering due to composition fluctuations is in general completely polarised. In spite of the appreciable size of the molecular clusters in glass, the value of ρ_u is diminished by the presence of this composition scattering. Glass can therefore be considered as a mixture of anisotropic molecular aggregates.

The influence of composition of the glass on the depolarisation value and intensity of scattering is very striking. The value of ρ_h is found to diminish with increasing percentage of acidic oxides such as silicon dioxide (SiO_2), boric oxide (B_2O_3), etc., in glass, whereas the value of ρ_h tends to increase as the proportion of basic oxides such as Na_2O, K_2O, PbO etc., increases. In other words, the tendency for the formation of large molecular aggregates is greater for glasses containing more of acidic oxides especially boric oxide and less of basic oxides than for glasses which contain more of basic oxides and less of acidic oxides. Glasses numbered 4, 5, 8, 10, 16 and 17 are illustrative of the above conclusions. The regularity in the dependence of scattering on composition makes it clear that the scattering phenomenon observed in optical glasses is not due to accidental inclusions but is an intrinsic property of glass.

The conclusions of the author regarding the constitution of glass fully substantiate the remarks made by G. Hagg[7] in his paper on the "Nature of Vitreous State". His remarks can be summarised in a few words as follows :—Glass is an aggregate of large groups. A melt will show tendency for glass formation if it contains large and irregular groups of molecules. The only oxides which are known in the vitreous state are B_2O_3, SiO_2, P_2O_3,

[7] G. Hagg, *Journ. of Chem. Phys.*, 1935, 3, 42.

P_2O_5, GeO_2, As_2O_3 and As_2O_5. A melt containing any one of these oxides will easily tend to become glassy on cooling. Glass forming tendency is largest for boric oxide (B_2O_3), which cannot even be obtained in crystalline form. The glass forming ability of the melt will decrease when it is getting more basic.

7. *Conclusion.*

Important information concerning the constitution of glass and the nature of the vitreous state in general may be expected to result from a detailed study of the Raman spectra as they offer a unique method of investigating these substances which give no X-ray pattern and which will not yield to the usual physico-chemical method of approach. Notwithstanding the inherent difficulties, considerable progress has been made in this direction by Gross and Romanova,[8] Hollaender and Williams,[9] Bhagavantam[10] and by Kujuinzelis.[11] The Raman lines obtained from glasses are in general broad and diffuse. In addition to these diffuse lines, there is a general background scattering. Consequently the interpretation of the Raman spectra obtained has not been easy. The broadening of the lines as well as the frequency shifts are attributed to the influence of polymerisation. It appears possible that a connection may exist between the width of the Raman bands and the clustering tendency disclosed by the present investigation. Further experimental work in this direction appears desirable.

In conclusion the author takes this opportunity to record his grateful thanks to Prof. Sir C. V. Raman, KT., F.R.S., N.L., under whose guidance the present investigation was carried out.

8. *Summary.*

A comparative study has been made of the intensity and state of polarisation of the light scattered transversely by a series of seventeen glasses of optical quality with the incident light in different states of polarisation (namely, unpolarised, vertically polarised and horizontally polarised). A weak fluorescence was observed in all the glasses. Measurements of the depolarisation factors ρ_u, ρ_v and ρ_h were made with an orange filter in the path of the incident beam to eliminate fluorescence. ρ_u and ρ_v are found to be of the same order of magnitude as are usually observed in the case of gases. But on the other hand, ρ_h is found to be distinctly less than 100%

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[8] E. Gross and M. Romanova, *Zeits. fur Phys.*, 1929, **55**, 744.

[9] A. Hollaender and J. W. Williams, *Phys. Rev.*, 1929, **34**, 380; 1931, **38**, 1739.

[10] S. Bhagavantam, *Ind. Journ. of Phys.*, 1931, **6**, 1.

[11] Th. G. Kujuinzelis, *Zeits. fur Phys.*, 1935, **97**, 561.

showing thereby the existence of molecular aggregates of size not small compared with the wavelength of light. Since no visible inclusions are observed it is concluded that the scattering in glass is really an internal phenomenon. Measurements of the relative intensity of scattering in these glasses were also made employing the photo-electric method. The influence of composition of the glass on the formation and the size of the molecular aggregates formed is fully discussed. It is found that the tendency for the formation of molecular aggregates increases with an increasing percentage of acidic oxides especially boric oxide, whereas it diminishes when the glass gets more and more basic.

GRAVITY FORMULÆ IN GEODESY; THEIR PRECISION AND INTERPRETATION.

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Various formulæ for gravity have been introduced from time to time by different geodesists with the result that up till recently, the different countries expressed their gravity anomalies in different terms. Such a state of affairs was obviously highly undesirable for a research into the figure of the Earth, and other correlated problems, where collated data over the whole globe is required. This led to a resolution at the International Union of geodesy and geophysics at Prague (1927), that the advisability of adopting an International gravity formula should be considered, and that such a gravity formula should be brought forward. Although opinions were divided whether in view of the paucity of gravity data, time was ripe for such a gravity formula, still everybody was at one, that uniformity was essential, and that different countries should use the same gravity formula. The International gravity formula was proposed by Heiskanen, and was adopted by the International Union at Stockholm in 1930. This is however not the last word, as Helmert's 1901 and 1915, and Bowie's 1927 formulæ are still in vogue, and there is no doubt that a better formula will be derived when more gravity data are available. Tables have been made for the conversion of gravity from one spheroid to the other. The literature about the derivation of these formulæ is very scattered, and in most cases is not easily accessible, and consequently it is not often realised, that the various formulæ have been derived from quite different considerations.

The object of this paper is to enumerate the important gravity formulæ, and outline the methods of their derivation, discussing the degrees of approximation involved, as well as the interpretation of the various terms.

The following are the main gravity formulæ obtained at different times :—

Helmert 1901. $\gamma_0 = 978{\cdot}030\,[1 + 5302\times10^{-6}\sin^2\phi - 7\times10^{-6}\sin^2 2\phi]$ .. (1)

$$\epsilon = \frac{1}{298{\cdot}3} = 0{\cdot}003354, \quad f = -205\times10^{-8}.$$

Helmert 1915. $\gamma_0 = 978{\cdot}052\ [1 + \underset{\pm 7}{5285} \times 10^{-6} \sin^2\phi - 7 \times 10^{-6} \sin^2 2\phi$

$+ \underset{\pm 4}{18} \times 10^{-6} \cos^2\phi \cos 2\ (L + \underset{\pm 6}{17}^\circ)]$ .. .. (2)

$\epsilon = 0{\cdot}00371 + 18 \times 10^{-6} \cos^2\phi \cos 2\,(L + 17^\circ),$

Average $\epsilon = \frac{1}{296{\cdot}7}$, $f = -205 \times 10^{-8}$

Berroth. $\gamma_0 = \underset{\pm 4{\cdot}4}{978{\cdot}046}\ [1 + \underset{\pm 7{\cdot}7}{5296} \times 10^{-6} \sin^2\phi + 11{\cdot}6$

$\times 10^{-6} \cos^2\phi \cos 2\ (L + 10^\circ) - 7 \times 10^{-6} \sin^2 2\phi]$ .. (3)

$\epsilon = \frac{1}{297{\cdot}8 \pm 0{\cdot}7} + 11{\cdot}6 \times 10^{-6} \cos 2\ (L + 10^\circ),$

$f = -205 \times 10^{-8}$

Bowie 1917. $\gamma_0 = 978{\cdot}039\ [1 + 5294 \times 10^{-6} \sin^2\phi - 7 \times 10^{-6} \sin^2 2\phi]$ .. (4)

$\epsilon = \frac{1}{297{\cdot}4 \pm 1{\cdot}0}$, $f = -205 \times 10^{-8}$

Survey of India, Spheroid II.[1]

$\gamma_0 = 978{\cdot}021\ [1 + 5234 \times 10^{-6} \sin^2\phi - 6 \times 10^{-6} \sin^2 2\phi]$ .. (5)

$\epsilon = \frac{1}{292{\cdot}4}$, $f = 0$

Best formula for India as available from data till 1929 is

$\gamma_0 = 978{\cdot}021\ [1 + 5359 \times 10^{-6} \sin^2\phi - 6 \times 10^{-6} \sin^2 2\phi]$ .. (6)

$\epsilon = \frac{1}{301}$, $f = 0$

Heiskanen 1924. $\gamma_0 = \underset{\pm 3}{978{\cdot}052}\ [1 + \underset{\pm 6}{5285} \times 10^{-6} \sin^2\phi + \underset{\pm 3}{27} \times 10^{-6} \cos^2\phi$

$\times \cos 2\ (L - \underset{\pm 5}{18}^\circ) - 7 \times 10^{-6} \sin^2 2\phi]$ .. (7)

Average $\epsilon = \frac{1}{296{\cdot}7 \pm 0{\cdot}5}$, $f = -205 \times 10^{-8}$

Heiskanen 1928. $\gamma_0 = 978{\cdot}049\ [1 + 5293 \times 10^{-6} \sin^2\phi - 7 \times 10^{-6} \sin^2 2\phi$

$+ 19 \times 10^{-6} \cos^2\phi \cos 2\ (L - 0^\circ)]$ .. .. (8)

Average $\epsilon = \frac{1}{297{\cdot}3}$, $f = -205 \times 10^{-8}$

International ellipsoid

$\gamma_0 = 978{\cdot}049\ [1 + 52884 \times 10^{-7} \sin^2\phi - 59 \times 10^{-7} \sin^2 2\phi]$ .. (9)

$\epsilon = \frac{1}{297}$, $f = 0$

ϕ and L are the geodetic latitude and longitude. Longitudes are reckoned positive E. of Greenwich meridian. ϵ denotes the ellipticity of the spheroid. Meaning of f is made clear later.

There are two main directions, into which the body of research into gravity formulæ may be branched. One is the classical method of Stokes[2], Helmert[3] and Darwin[4], the other is the modern work of Pizetti, Cassinis and other Continental writers.

The historical method of approach consists in writing down the expression for external potential of an attracting system in the form of an infinite series by means of spherical harmonics. If the form of the geoid is

$$r = k\,(1 + u_2 + u_3 + \cdots\cdots) \qquad .. \qquad .. \qquad .. \quad (10)$$

and if there are no masses external to it, the potential due to it in external space is given by

$$U = \frac{y_0}{r} + \frac{y_1}{r^2} + \cdots\cdots$$

Using the condition that the geoid is an equipotential, namely

$$U + \tfrac{1}{2}\,\omega^2\, r^2 \cos^2\theta = c,$$

Stokes derived the following expression for U.

$$U = \frac{y_0}{r} + \frac{k y_0 u_1}{r^2} + \cdots\cdots - \frac{\omega^2\, k^5}{2r^3}\,(\tfrac{1}{3} - \sin^2\theta), \qquad .. \quad (11)$$

where θ denotes the geocentric latitude.

The force of gravity at a point of the geoid is given by differentiating (11) with respect to an element of normal of the geoid. To a first approximation we may take

$$g = -\frac{d}{dr}\,(U + \tfrac{1}{2}\,\omega^2\, r^2 \cos^2\theta).$$

This fixes the value of gravity on the geoid to be

$$g = G\,[1 - \tfrac{5}{2}\,m\,(\tfrac{1}{3} - \sin^2\theta) + u_2 + 2u_3 + \cdots\cdots + (n-1)u_n + \cdots\cdots] \quad .. \quad (12)$$

$$\left.\begin{aligned} \text{where } m &= \frac{\omega^2\, k}{G}, \quad y_0 = k\left(c - \frac{\omega^2\, k^2}{3}\right), \\ \text{and} \quad G &= \frac{\iint g\, d\omega}{4\pi} = \frac{y_0}{k^2} - \tfrac{2}{3}\,\omega^2 k = \frac{1}{k}\,(c - \omega^2 k^2). \end{aligned}\right\} \qquad .. \qquad .. \quad (13)$$

The equation of a spheroid correct to first order in ellipticity is

$$r = a\,(1 - \epsilon \sin^2\theta) = k\,(1 - \tfrac{2}{3}\,\epsilon\, P_2),$$

where $\epsilon = \dfrac{a-b}{a}$, a and b being the semi-axes. k is the radius of a sphere of equal volume.

From (12) we see that gravity on a spheroid is

$$g = G\,[1 - (\tfrac{5}{2}\,m - \epsilon)\,(\tfrac{1}{3} - \sin^2\theta)] \quad .. \quad .. \quad .. \quad (14)$$

If ϕ is the geodetic latitude, then $\theta = \phi - \epsilon \sin 2\phi$, ... (15)

and we get $g = G_e\,(1 + A \sin^2 \phi)$,

where G_e denotes gravity at the equator, and

$$A = (\tfrac{5}{2}\,m - \epsilon)$$

Helmert applied (15) to the gravity data at his disposal, and by a least square solution found $A = 0{\cdot}0052$, and $G_e = 978{\cdot}06$ gals.

We will now discuss the accuracy of this formula.

The correct expression for gravity is

$$g = -\frac{d}{dn}\,(U + \tfrac{1}{2}\,\omega^2 r^2 \cos^2\theta),$$

the differentiation being along the normal to the spheroid.

If ψ is the small angle between the spheroidal normal and the radius vector at any point P, the error $= -g_n + g = g_n\,(\cos\psi - 1) = -g_n \dfrac{\psi^2}{2}$,

where $\psi = \epsilon \sin 2\phi + \ldots\ldots$

Hence the error is of the order $G\epsilon^2 = \dfrac{1000}{9 \times 10^4} = 0{\cdot}011$ gals.

This is rather large, considering that nowadays gravity can easily be measured with a probable error of 1 or 2 milligals.

The equation of the spheroid being limited to first order terms in ϵ, the error of the radius vector is of order

$$a\,\epsilon^2 = \frac{20 \times 10^6}{9 \times 10^4} \doteqdot 200 \text{ feet.}$$

In geodesy, this spheroid is used as a reference figure to fix the geoid from which it differs by small amount. An error of 200 feet in the dimensions of the reference figure is not admissible.

Equation (12) has been derived from first order considerations only, terms of second order being neglected.

If the figure of the Earth is a triaxial ellipsoid, the mean ellipticity of whose meridians is ϵ, and the ellipticity of whose equator is η, its polar equation may be written as

$$r = k\left\{1 + \epsilon\,(\tfrac{1}{3} - \sin^2\theta) + \frac{\eta}{2}\cos 2\,(L - L_0)\cos^2\theta\right\}, \quad .. \quad (16)$$

where L_0 is the longitude, in which the semi-major axis lies.

This is derived from (9) by putting

$$u_1 = 0 \text{ and } u_2 = \epsilon\,(\tfrac{1}{3} - \sin^2\theta) + \tfrac{1}{2}\,\eta \cos 2\,(L - L_0)\cos^2\theta$$

Hence gravity on it would be

$$g = G\left\{1 + (\epsilon - \tfrac{5}{2}m)(\tfrac{1}{3} - \sin^2\theta) + \frac{\eta}{2}\cos^2\theta\cos 2\ (L - L_0)\right\} \quad .. \quad (17)$$

Gravity formulæ (2), (3), (7) and (8) enumerated above are of this form, and therefore they show that the geoid has the form of a triaxial ellipsoid. It might be mentioned here, that the theory of rotating fluids shows that a triaxial fluid ellipsoid having the velocity, density and dimensions of the earth cannot be in equilibrium. For the earth, both the meridional and equatorial sections are nearly circular, and have a small ellipticity, while the equilibrium ellipsoid cannot have both of its elliqticities small. Hence adoption of a triaxial form of the geoid is contrary to theory.

It was soon realised that the above formulæ were inadequate to satisfy the practical requirements of geodesy, and Helmert and Darwin then proceeded to get the gravity formulæ correct to second order terms in ellipticity. They proceeded along practically identical lines. A short outline of their method is desirable, indeed necessary for a true appreciation of the formulæ.

The potential W_P at a point P external to the geoid due to attracting masses within the geoid is

$$W_P = \iiint \frac{dm}{\sqrt{R^2 + r^2 - 2Rr\cos\zeta}}$$

$$= \sum_{n=0} \frac{y_n}{r^{n+1}} \text{ for } R > r, \quad .. \quad .. \quad .. \quad (18)$$

where $$y_n = \int_{r=0}^{\text{geoid}} r^n P_n\, dm \quad .. \quad .. \quad .. \quad .. \quad (19)$$

R, r are the distances of the point P and an element of attracting mass dm from the centre of mass, and ζ is the angle between the directions of R and r. Choosing origin at the centre of mass of the attracting masses, and axes of inertia as the axes of co-ordinates, the first three terms of (18) can easily be evaluated.

Let (x, y, z) be the cartesian co-ordinates, and (θ, λ) the geocentric latitude and longitude of an element dm of attracting mass.

Now $P_0 = 1$

$$P_1 = \sin\theta\sin\theta_0 + \cos\theta\cos\theta_0\cos(\lambda - \lambda_0)$$

$$P_2 = \tfrac{3}{4}(\sin^2\theta - \tfrac{1}{3})(\sin^2\theta_0 - \tfrac{1}{3}) + 3\sin\theta\cos\theta\sin\theta_0\cos\theta_0\cos(\lambda - \lambda_0) + \tfrac{3}{4}\cos^2\theta\cos^2\theta_0\cos 2(\lambda - \lambda_0),$$

and so on.

By our choice of origin and axes of co-ordinates

$\int x dm = \int r \cos\theta \cos\lambda \, dm = 0$. Similarly $\int y dm = \int z dm = 0$

$\int xy dm = \int yz dm = \int zx dm = 0$

$$A = \int (y^2 + z^2)\, dm,\ B = \int (z^2 + x^2)\, dm,\ C = \int (x^2 + y^2)\, dm.$$

or $$\int x^2\, dm = \frac{C - A + B}{2}, \text{ etc.}$$

Hence from (19), $y_0 = M$, the total mass of geoid,

$$y_1 = \int r\, P_1\, dm = 0$$

$$y_2 = \int r^2\, P_2\, dm = \tfrac{3}{2}\left(\frac{A+B}{2} - C\right)(\sin^2\theta_0 - \tfrac{1}{3}) + \tfrac{3}{4}(B - A) \times \cos^2\theta_0 \cos 2\lambda_0.$$

Evaluation of y_3 and subsequent terms becomes very complicated.

Hence $$W = \frac{M}{r}\left\{1 - \tfrac{3}{2}\frac{K}{r^2}(\sin^2\theta - \tfrac{1}{3}) + \tfrac{3}{4}\frac{B-A}{Mr^2}\cos^2\theta \cos 2\lambda\right\} + \frac{y_3}{r^3} + \frac{y_4}{r^4} + \ldots\ldots + \tfrac{1}{2}\omega^2 r^2 \cos^2\theta, \quad .. \quad .. \quad .. \quad (20)$$

where $K = \frac{1}{M}\left(\frac{A+B}{2} - C\right)$.

This expression holds for any rotating body.

For a homogeneous spheroid $\frac{x^2+y^2}{a^2} + \frac{z^2}{b^2} = 1$,

$$A = B = \frac{M}{5}(a^2 + b^2),\ C = \tfrac{2}{5} M a^2,$$

hence $K = -\frac{a^2 e^2}{5}$, where e is the eccentricity.

The third term obviously vanishes. y_3 is also zero.

$$y_4 = \int P_4\, r^2\, dm = \frac{a^4 e^4}{280}(105 \sin^4\phi - 90 \sin^2\phi + 9).$$

We thus deduce the potential of a spheroid to be

$$W = \frac{M}{r}\left\{1 + \frac{a^2 e^2}{10 r^2}(1 - 3\sin^2\phi) + \frac{a^4 e^4}{280 r^4}(105 \sin^4\phi - 90 \sin^2\phi + 9) + \ldots\right\}.$$

Helmert assumed in the first instance that the potential of the earth instead of being represented by (19) was

$$U = \frac{M}{r}\left\{1 - \tfrac{3}{2}\frac{K}{r^2}(\sin^2\theta - \tfrac{1}{3}) + \tfrac{3}{4}\frac{B-A}{Mr^2}\cos^2\theta \cos 2\lambda + \frac{\omega^2 r^3}{2M}\cos^2\theta\right\} \quad .. \quad (21)$$

W and U are nearly equal. The equipotentials, U = constant, are known as "level spheroids". It might be pointed out, that these surfaces are not

actual spheroids, but are fairly close approximations to them. Also A, B have now lost their physical significance. They are no more the exact moments of inertia of the masses within the geoid. On these level spheroids, gravity is given by

$$g = \frac{M}{r^2}\left\{1 + \frac{3K}{2r^2}(1 - 3\sin^2\theta) + \frac{9(B - A)}{4Mr^2}\cos^2\theta\cos 2\lambda - \frac{\omega^2 r^3}{M}\cos^2\theta\right\}$$

This formula has never been much in vogue.

Helmert next took as an approximation to W,

$$U = \frac{M}{r}\left\{1 + \frac{K}{2r^2}(1 - 3\sin^2\theta) + \frac{\omega^2 r^3}{2M}\cos^2\theta + \frac{D}{r^4}(\sin^4\theta - \tfrac{6}{7}\sin^2\theta + \tfrac{3}{35})\right\} \ldots (22)$$

On reference to (18), we see that only those terms of y_4 have been included, which are independent of λ. The whole of y_4 has not been included, as the equipotentials are intended to be symmetrical with respect to the rotation axis. The y_3 term has also been omitted for the same reason. Neglecting the term containing the angular velocity, formula (22) resembles exactly the expression for the potential of a spheroid at an external point, namely

$$U = \frac{M}{r}\left\{1 + \frac{a^2 e^2}{10 r^2}(1 - 3\sin^2\theta) + \frac{a^4 e^4}{280 r^4}(105\sin^4\theta - 90\sin^2\theta + 9) + \cdots\right\}.$$

Let the polar equation of a meridian curve of the equipotential surface

$$u + \tfrac{1}{2}\omega^2 r^2 \sin^2\theta = u_0$$

be $$r = a(1 - P\sin^2\theta + Q\sin^4\theta - \cdots) \quad \ldots \quad \ldots \quad \ldots (23)$$

Substituting in (22), and using (23), we see that

$$a = \frac{M}{u_0}\left\{1 + \frac{K}{2a^2} + \frac{\omega^2 a^3}{2M} + \frac{3D}{35 a^4}\right\}$$

$$P = \frac{M}{a u_0}\left\{\frac{K}{a^2}(\tfrac{3}{2} - P) + \frac{\omega^2 a^3}{2M}(1 + 3P) + \tfrac{6}{7}\frac{D}{a^4}\right\}$$

$$Q = \frac{M}{a u_0}\left\{P\left(\tfrac{3}{2}\frac{\omega^2 a^3}{M} - \frac{3K}{a^2}\right) + \frac{D}{a^4}\right\}$$

Since, we are now aiming at accuracy upto second order of small quantities, we have to take

$$g^2 = U_1^2 + U_2^2, \text{ where } U_1 = -\frac{\delta}{\delta r}(U + \tfrac{1}{2}\omega^2 r^2\cos^2\theta),\ U_2 = -\frac{\delta}{r\delta\theta}(U + \tfrac{1}{2}\omega^2 r^2\cos^2\theta).$$

It is found after easy simplification, that the equation of the meridian curve is

$$r = a\{1 - (\epsilon - 2\epsilon^2 + \tfrac{5}{2}\epsilon m + \delta)\sin^2\theta - (2\epsilon^2 - \tfrac{5}{2}\epsilon m - \delta)\sin^4\theta\} \ldots (24)$$

and gravity on it is

$$g = G_e\left\{1 + (\tfrac{5}{2}m - \epsilon + 6\epsilon^2 - \frac{\epsilon m}{2} - \tfrac{19}{7}\delta)\sin^2\theta - (7\epsilon^2 - 3\delta)\sin^4\theta\right\} \ldots (25)$$

where G_e is the mean value of gravity on the equator,

$$\left.\begin{aligned} G_e &= \frac{M}{a^2}\left\{1+\epsilon-\frac{3m}{2}-\epsilon^2-\tfrac{1}{2}\epsilon m+\tfrac{9}{4}m^2+\tfrac{4}{7}\delta\right\} \\ m &= \frac{\omega^2 a}{G_e} \\ \delta &= \frac{D}{a^4} \\ \frac{3K}{2a^2} &= \epsilon-\frac{m}{2}-\epsilon^2+\tfrac{1}{2}\epsilon m+\tfrac{3}{4}m^2+\tfrac{4}{7}\delta \end{aligned}\right\} \quad .. \quad .. \quad .. \quad (26)$$

To express (25) in terms of geodetic latitude ϕ, we make use of the relation $\theta = \phi - \epsilon \sin 2\phi$, and get

$$g = G_e\,(1 + A \sin^2\phi - B \sin^2 2\phi), \quad .. \quad .. \quad .. \quad (27)$$

where
$$\left.\begin{aligned} A &= \tfrac{5}{2}m-\epsilon-\epsilon\left(\epsilon+\frac{m}{2}\right)+\tfrac{3}{7}\delta \\ B &= -\frac{7\epsilon^2-3\delta}{4}+\epsilon A \end{aligned}\right\} \quad .. \quad .. \quad .. \quad (28)$$

By giving different values to δ in (24) we can get the formula for gravity on an equipotential surface having a known form differing but little from an ellipsoid of revolution.

Darwin's method is practically identical. He starts with a level surface

$$r = a\,\{1 - \epsilon \sin^2\theta + (f - \tfrac{3}{2}\epsilon^2) \sin^2\theta \cos^2\theta\} \quad .. \quad .. \quad (29)$$

and writes its external potential as

$$U = \frac{M}{r} + \frac{\beta P_2}{r^3} + \frac{\gamma P_4}{r^5} \quad .. \quad .. \quad .. \quad .. \quad (30)$$

The two equations (24) and (29) are identical, if

$$f = \tfrac{7}{2}\epsilon^2 - \tfrac{5}{2}m\epsilon - \delta.$$

Proceeding exactly as before Darwin arrived at the equations (27) and (28). In getting g, he also used

$$g^2 = U_1^2 + U_2^2$$

In actual practice, the situation is, that gravity is observed on the earth, and by some suitable method, it is reduced to the geoid. From these values of gravity, the shape of the geoid has to be deduced. We have seen that on the level surface (24),

$$g = G_e\,[1 + A \sin^2\phi - B \sin^2 2\phi],$$

where the quantities G_e, A and B are expressible in terms of M, m, ϵ, and δ.

A knowledge of the values of gravity at three places will give us G_e, A and B. However, to obtain reliable values for these constants, they are determined by least squares using as many gravity stations as are available.

B is a small quantity, about $\frac{1}{800}$ times smaller than A, and it was found that its value could not be deduced from the gravity data with any accuracy.

The quantity δ defines the elevation or depression of reference surface (24) from a true spheroid, and is determined from theoretical considerations. Darwin has deduced values of δ (or f) from two quite different assumptions about the internal constitution of the earth. He first assumed Roche's law of density, and obtained $f = -205 \times 10^{-8}$. Then he used Wiechert's law, that the earth consists of a solid core of density 8·206, on which is superposed a mantle of density 3·2, and deduced $f = -175 \times 10^{-8}$. The constant B in the gravity formula expressed in terms of f may be written as

$$B = -\frac{\epsilon^2}{8} + \frac{5\,m\,\epsilon}{8} - \frac{3f}{4}.$$

Taking $f = -205 \times 10^{-8}$, $m = \frac{1}{288 \cdot 41}$, and $\epsilon = \frac{1}{298}$,

we get $B = 7 \times 10^{-6}$.

Hence the quantity $7 \times 10^{-6} \sin^2 2\phi$, which occurs in all gravity formulæ is based on theoretical considerations. The magnitude of this term is of the order $7 \times 10^3 \times 10^{-6} \sin^2 2\phi$. The maximum value that it can attain is 0·007, which is quite appreciable.

Darwin's work shows that the figure 7×10^{-6} for B is quite insensitive to the hypothesis about the internal constitution of the earth. It corresponds to a geoid depressed below an exact spheroid by about 3^m in latitude 45°. Considering, however, that it is derived from hypothetical assumption about the variation of density in the earth's crust, it appears a bit pedantic to retain it.

For an exact spheroid, which can be used as reference figure for the earth, $B = 6 \times 10^{-6}$ as we shall show later. This value has been used in the International formula.

Yet another approximation may be taken for W, namely

$$U = \frac{M}{r}\left[1 + \frac{K}{2r^2}(1 - 3\sin^2\theta) + \frac{\omega^2 r^3}{2M}\cos^2\theta + \frac{L}{r^2}\cos^2\theta \cos 2(L - L_0)\right.$$
$$\left. + \frac{T}{r^3}\left(\tfrac{3}{5}\sin\theta - \sin^3\theta\right) + \frac{D}{r^4}\left(\sin^4\theta - \tfrac{6}{7}\sin^2\theta + \tfrac{3}{5}\tfrac{3}{5}\right)\right] \quad .. \quad .. \quad (31)$$

Gravity on a level surface whose potential is as above is

$$g = G_e\left\{1 + (\beta_2 + \beta_4)\sin^2\phi + \beta'_2 \cos^2\phi \cos 2(L - L_0) + \beta_3\left(\tfrac{3}{5}\sin\phi - \sin^3\phi\right)\right.$$
$$\left. - \frac{\beta_4}{4}\sin^2 2\phi\right\} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (32)$$

The equation of the meridian curve is

$$r = a_m \{1 - \alpha \sin^2\phi + \beta \cos^2\phi \cos 2(L_c - L_0) + \gamma (\tfrac{3}{5} \sin\phi - \sin^3\phi) + \delta \sin^2 2\phi\} \quad (33)$$

It can be easily verified that these results agree with Stokes' equations, namely that for

$$g = G [1 + u_2 + u_3 + \cdots\cdots],$$

$$r = R [1 + \tfrac{5}{2} m (\tfrac{1}{3} - \sin^2\phi) + u_2 + \tfrac{1}{2} u_3 + \cdots\cdot].$$

The equation to r contains $(\frac{3}{5} \sin\phi - \sin^3\phi)$. If the northern and southern hemispheres are symmetrical, this term should disappear in r, and therefore also in g.

β'_2 is a function of difference (B − A) of the moments of inertia of the level surface.

The rigid theory of triaxial ellipsoid gives (as we shall see later),

$$g = g_a \left[1 + \tfrac{1}{4}(e'^2 + 2\eta') + \left\{\tfrac{1}{2}(e^2 + 2\eta) + \frac{e^2}{8}(3e^2 + 4\eta) - \tfrac{1}{4}(e'^2 + 2\eta')\right\} \sin^2\phi \right.$$

$$\left. - \tfrac{1}{4}(e'^2 + 2\eta') \cos^2\phi \cos 2L_c - \frac{e^2}{32}(3e^2 + 4\eta) \sin^2 2\phi\right] \quad .. \quad (34)$$

In (34), $g_e = g_a \{1 + \tfrac{1}{4}(e'^2 + 2\eta')\}$

For Helmert's 1915 formula, $g_e = 978{\cdot}052$,

and $-\tfrac{1}{4}(e'^2 + 2\eta') = +18 \times 10^{-6}$,

hence $978{\cdot}052 = g_a (1 - 18 \times 10^{-6})$

or $g_a = 978{\cdot}052 (1 + 18 \times 10^{-6}) = 978{\cdot}070$

where g_a is gravity at the extremity of the semi-major axis.

978·052 is mean value of gravity at the equator.

At the equator, $g = g_a [1 + \tfrac{1}{4}(e'^2 + 2\eta') - \tfrac{1}{4}(e'^2 + 2\eta') \cos 2L_c]$

Mean equatorial gravity $= g_a [1 + \tfrac{1}{4}(e'^2 + 2\eta')]$.

The second method, and one which is more fundamental is the one propounded by Pizetti[5] in 1913. It deals with the case of a triaxial ellipsoid, which is a level surface of its own attraction and rotation. Strictly speaking, the assumption that a level surface is an exact ellipsoid is inconsistent with perfect hydrostatic equilibrium, as has been remarked already. Somgliana proceeding on the same lines as Pizetti derived a closed elegant expression for gravity on an ellipsoid, which may be written as

$$g = \frac{(ag_a \cos^2 L_c + bg_b \sin^2 L_c) \cos^2\phi + cg_c \sin^2\phi}{\sqrt{(a^2 \cos^2 L_c + b^2 \sin^2 L_c) \cos^2\phi + c^2 \sin^2\phi}} \quad .. \quad .. \quad (35)$$

where g_a, g_b, g_c are the values of g at the extremities of the three axes, and (ϕ, L_c) denote the latitude and longitude respectively.

This can be easily verified, because the 3 extremities of the axes are given by ($\phi = 0$, $L_1 = 0$), ($\phi = 0$, $L_1 = 90°$), and $\phi = 90°$ and when these values are substituted in (35), g assumes the appropriate values.

Somigliana in No. 38 of *Bulletin Geodesique*, 1933 has expanded (35) and has obtained

$$g = g_a \left[1 + \tfrac{1}{2}(e^2 + 2\eta)\sin^2\phi + \tfrac{1}{2}(e'^2 + 2\eta')\cos^2\phi \sin^2 L_1 + \frac{e^2}{2\cdot 4}(3e^2 + 4\eta)\sin^4\phi\right], \quad .. \quad (36)$$

where $e^2 = \dfrac{a^2 - c^2}{a^2}$, $\quad e'^2 = \dfrac{a^2 - b^2}{a^2}$,

$$\eta = \frac{cg_c - ag_a}{ag_a}, \quad \eta' = \frac{bg_b - ag_a}{ag_a}.$$

For a spheroid, η' and e' become zero, and the L_1-term disappears.

For a spheroid, $g = \dfrac{ag_e \cos^2\phi + cg_p \sin^2\phi}{\sqrt{a^2\cos^2\phi + c^2\sin^2\phi}}$, where g_e, g_p denote the values of gravity at the extremities of the equatorial and polar axes.

$$g = G_e \frac{1 + (\beta - \epsilon - \epsilon\beta)\sin^2\phi}{\sqrt{1 - \epsilon(2-\epsilon)\sin^2\phi}}$$
$$= G_e[1 + \beta\sin^2\phi - \beta_1 \sin^2 2\phi - \beta_2 \sin^2\phi \sin^2 2\phi - \beta_3 \sin^4\phi \sin^2 2\phi - \cdots] \quad .. \quad (37)$$

where
$$\epsilon = \frac{a-c}{a}$$
$$\beta = \frac{g_p - g_e}{g_e} = \tfrac{5}{2} m\left(1 - \tfrac{17}{35}\epsilon - \cdots\right) - \epsilon \quad .. \quad .. \quad (38)$$
$$\beta_2 = \frac{\epsilon^2}{8}(2\epsilon + 3\beta) - \frac{\epsilon^3}{32}(3\epsilon + 4\beta).$$
. . . . . .

If we introduce an auxiliary parameter

$\eta = \dfrac{cg_p - ag_e}{ag_e}$ instead of β we can write (37) in the form

$$g = g_e\left[1 + \tfrac{1}{2}(e^2 + 2\eta)\sin^2\phi + \frac{e^2}{2\cdot 4}(3e^2 + 4\eta)\sin^4\phi + \cdots\right] \quad .. \quad (39)$$

W. D. Lambert in *Bulletin Geodesique*, 1931, has introduced another auxiliary function C, and has obtained an expression for g in the form

$$g = G_e(1 + C_2\sin^2\phi + C_4\sin^4\phi + \cdots), \quad .. \quad .. \quad (40)$$

where $C_2 = \tfrac{1}{2}(2mC - e^2) = \tfrac{1}{2}(e^2 + 2\eta)$

$$C_4 = \frac{e^2}{8}(4mC - e^2), \text{ etc.}$$

and $$C = \frac{\eta}{m} + e^2.$$

$$\epsilon + \beta = \tfrac{5}{2} \frac{\omega^2 a}{G_e} \chi(\epsilon) = \tfrac{5}{2} \frac{\omega^2 a}{G_e} (1 - \epsilon) C(e^2),$$

$$\chi(\epsilon) = 1 - \tfrac{17}{35} \epsilon - \frac{\epsilon^2}{245} - \cdots.$$

Formula (37) agrees exactly with Helmert's formula (27), except that it contains terms beyond the third. It can be easily verified that the constants A and B in the two formulæ are identical to the second order of small quantities.

It has been mentioned above that the constants A and G_e are derived from a least square solution, and B is determined from the theoretical value of f. Knowing A, B and δ, we can determine the values of ϵ and m from (24). When m is known, we can get a from the equation $m = \frac{\omega^2 a}{G_e}$, and it appears at first sight that g data provide information not only about the shape of the geoid, but also about its dimensions. The value of a so found is however useless, as m is a small quantity, which gets multiplied by a large number $\frac{G_e}{\omega^2}$, and thus the uncertainty in m is considerably magnified.

Knowing m and ϵ, we see from the equation

$$G_e = \frac{M}{a^2}\left[1 + \epsilon - \frac{3m}{2} + \epsilon^2 - \tfrac{27}{14} m\epsilon + \tfrac{9}{4} m^2\right], \quad \ldots \quad \ldots (41)$$

that G_e fixes the mass of the earth, and hence its mean density. Amongst the constants in the formula for normal gravity, this is the most important, and has a much greater effect than the others. A glance at the various g formulæ would show that very discrepant values have been obtained for it according to the location and extent of the g data used. The range of values is from 978·021 to 978·052.

Silva in *Accad. Nazionale dei Lincei*, 1930, suggested that $G_e = 978{\cdot}049$ was the best value, as it makes the mean observed value of gravity equal to the computed mean value. This was adopted at the International Union of geodesy and geophysics at Stockholm in 1930.

Taking $G_e = 978{\cdot}049$, $\epsilon = \frac{1}{297}$ and $m = \frac{1}{288{\cdot}36}$, (41) gives the mass of the earth to be 588×10^{19} tons. If we take the mean radius of the earth to be 6,371,221·3 metres we get its mean density to be 5·517 gm/cm³.

The values of G_e found so far show a range of 32 milligals. This corresponds to an uncertainty of $\frac{1}{30,000}$ in the mass and mean density of the earth.

It has been mentioned by Cassinis that once G_e is fixed, it is immaterial, whether we use a reference spheroid, or a triaxial ellipsoid with approximately the same meridional ellipticity, and small equatorial flattening.

The reference spheroid chosen is, however, of extreme importance. Values of normal gravity are widely different for different spheroids.

Thus, for Helmert's spheroid (1901), $\epsilon = \frac{1}{298 \cdot 3}$ and $A = 5302 \times 10^{-6}$

and for Bowie's spheroid, $\epsilon = \frac{1}{297 \cdot 4}$ and $A = 5294 \times 10^{-6}$.

The difference between the values of the constant A is small as the ellipticities of these spheroids are nearly equal. But for Clarke's 1880 spheroid, $\epsilon = \frac{1}{293}$ which gives $A = 5248 \times 10^{-6}$. The value of normal gravity on Clarke's spheroid can therefore differ from that on Helmert's spheroid by 0·050 gals. Table I shows the variation of the constant A with ϵ.

TABLE I.

$1/\epsilon$	A	$1/\epsilon$	A
290	$10^{-6} \times 5207$	296	$10^{-6} \times 5277$
291	$10^{-6} \times 5219$	297	$10^{-6} \times 5288$
292	$10^{-6} \times 5231$	298	$10^{-6} \times 5300$
293	$10^{-6} \times 5242$	299	$10^{-6} \times 5311$
294	$10^{-6} \times 5254$	300	$10^{-6} \times 5322$
295	$10^{-6} \times 5266$		

$m = \frac{\omega^2 a}{G_e}$, and strictly speaking, varies for each spheroid. Its approximate value is $\frac{1}{288}$. A change of 0·5 in $\frac{1}{m}$ produces a change of 0·014 gals. in γ_0, which is quite considerable. It is satisfactory to take m correct to 0·05. For the International spheroid, $m = \frac{1}{288 \cdot 36}$, and this value has been used in preparing the table. It is also useful to indicate the variation of A with G_e. A change of 1×10^{-3} in G_e corresponds to a change of $8 \cdot 85 \times 10^{-9}$ in A.

The first important thing to notice from gravity formulæ (2), (3), (7) and (8) is, that if we assume a triaxial ellipsoid with semi-axes a, b, c, (where $a > b > c$) as the equilibrium figure of the earth, then $g_c > g_a > g_b$, which is rather unexpected. At first sight, one would expect g_a to be less than g_b.

Next, a comparison of the formulæ (27) and (37) reveals the superiority of the second method over the first. If we start with the closed formula for gravity on a spheroid, we can expand it in series, and take as many terms as are necessary for the accuracy aimed at. To obtain terms beyond the third by the older method requires great labour. G. Cassinis[7] and W. D. Lambert[6] have published tables of the values of gravity on the International spheroid. The former has given two sets of tables, giving the numerical values of normal gravity to 3 and 4 places of decimals respectively. For this accuracy the formula

$$\gamma = 978{\cdot}0490\ (1 + 52884 \times 10^{-7} \sin^2 \phi - 59 \times 10^{-7} \sin^2 2\phi)$$

is sufficient.

W. D. Lambert has tabulated these values to six places of decimals, and has included the term $c \sin 6\phi$ in the formula.

It might be remarked however that with the present degree of accuracy of gravity measurements, the values of normal gravity to 6 decimal places are of academic interest only.

It is important to realise that the International formula is on a different footing to the others. Its dimensions $a = 637{,}838{\cdot}8$ metres and $\epsilon = \frac{1}{297}$ have been deduced from plumb-line deflections. The constants A and B have been computed by substituting these values in (28). The constant B in the other formulæ has been deduced from theoretical considerations involving assumptions about the internal constitution of the earth, and the constants G_e and A from least square solution.

The constants for International spheroid can be computed to any degree of accuracy that we like, but not so for the other formulæ.

Thus A $= 0{\cdot}005{,}288{,}38$
B $= 0{\cdot}000{,}005{,}87$
$\beta_2 = 0{\cdot}000{,}000{,}022$
} for the International spheroid.

In the older formulæ, the constants cannot be written to such numerical accuracy, as the probable error of their values deduced from least square solution is in the 5th place of decimals.

The values of ellipticity deduced from the different gravity formulæ have been given along with the formulæ. Its values range from $\frac{1}{293}$ to $\frac{1}{300}$, showing that it is very sensitive to the distribution of gravity data. The value $\frac{1}{297}$ adopted for the International formula has been obtained from deflection data in U. S. only, which is only 1·6% of the area of the whole earth. It was adopted not for its own intrinsic merit, but simply (for want of a better value) to ensure uniformity in the expression of gravity anomalies in different countries.

The ideal condition for the determination of the ellipticity is a net of g stations uniformly distributed over the globe. This is a desideratum at present. There are hardly any gravity stations in the Southern hemisphere. Even in the Northern hemisphere, there are immense gaps. But the future outlook is very hopeful, as different countries are at the moment actively engaged in pendulum operations.

In the U. S. S. R., five hundred stations have been occupied within the last ten years, and their present output is about 1200 stations per year. Their objective is to cover Russia with a density of one station per 20 square Kms. With the advent of the static gravity meter, which is a marked improvement on the older pendulum apparatus as regards speed, and the success with the Vening Meinesz's apparatus for getting gravity at sea, time is not far, when the ideal distribution mentioned above will be achieved.

REFERENCES.

1. Survey of India, *Geodetic Report*, Vol. **V**, p. 55.
2. G. G. Stokes, *Mathematical and Physical Papers*, Vol. **II**, p. 131.
3. F. R. Helmert, *Hohere Geodesic*, Vol. **II**.
4. G. H. Darwin, *Scientific Papers*, Vol. **III**, p. 78.
5. P. Pizetti, "Principi della teoria meccanica della fijura d' equilibro dei pianeti," *Pisa, Spoerri*, 1913.
6. W. D. Lambert and F. W. Darling, *Bulletin Geodesique*, 1931, p. 327.
7. G. Cassinis, *Bulletin Geodesique*, 1931, p. 313.

DERIVATIVES OF SALICYLIC ACID.—PART IX.

Stability of the Sulphonic Acid Group in the 4-Sulphosalicylic Acid. Part I. Nitration of 4-Sulphosalicylic Acid.

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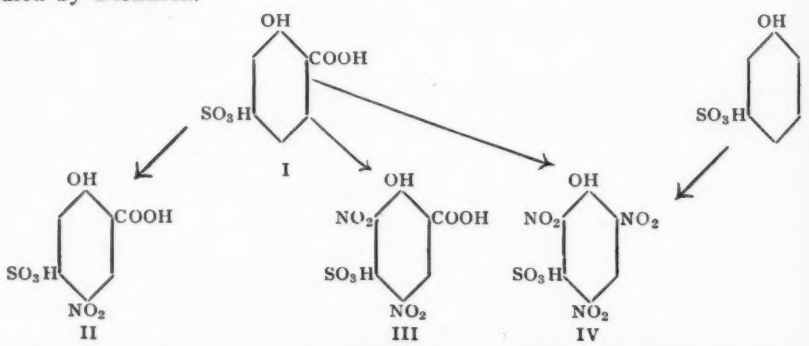
It has been found by the previous workers that the sulphonic acid group in either 3-sulpho- or 5-sulpho-salicylic acid can easily be substituted by the nitro group, and if the reaction is carried further, the -COOH group is removed and picric acid is the usual and the only product. Thus Datta and Varma[1] obtained picric acid by the action of nitrous gases on 5-sulpho-salicylic acid. Meldrum and Hirwe[2] obtained 3 : 5-dinitrosalicylic acid by controlled nitration of 5-sulphosalicylic acid.

With the view to study the stability of the sulphonic acid group in 4-sulphosalicylic acid (I), it was treated with nitric acid in acetic anhydride, when nitrosulphosalicylic acid (II) and dinitrosulphosalicylic acid (III) were obtained. On heating (I) with concentrated nitric acid symmetrical trinitro-*m*-phenol-sulphonic acid (IV) was obtained. A similar result was obtained by heating phenol-*m*-sulphonic acid with nitric acid, when a compound identical with (IV) was formed, the barium salt of which has been studied by Berndsen.[3]



Thus it can be seen that the sulphonic acid group is not always substituted by the nitro group but sometimes appears to be as stable as -COOH.

It enters easily and is as easily substituted when it occupies a position influenced by groups already present, but in positions outside this influence it is difficult to introduce and cannot be easily displaced.

The combined directing influence of the -OH and -COOH groups in salicylic acid is evident in many instances, as also the preference to position -5 over that of -3. When this fact is considered, the constitutions of the nitrosulpho compounds described above require no separate proof.

Respective amino compounds also have been obtained from them.

Experimental.

Nitration of 4-sulphosalicylic acid:—*4-Sulphosalicylic acid* was prepared as described in our previous paper.[4] It was dehydrated by keeping it over H_2SO_4 for two days.

Acid potassium-4-sulpho-5-nitrosalicylate:—To 4-sulphosalicylic acid (desiccated; 10 g.) dissolved in acetic anhydride (40 c.c.) and well cooled in ice, nitric acid (12 c.c.; sp. gr. 1·4) was slowly added below 5° and the mixture was left for twelve hours in a refrigerator and then at room temperature for twenty-four hours. The separated solid was found to be 4-sulpho-3 : 5-dinitrosalicylic acid. On diluting the mother liquor with concentrated potassium chloride solution, the acid potassium salt of 4-sulpho-5-nitrosalicylic acid (5·5 g.) was obtained. It crystallised from water in pale yellow plates. On further concentration of the mother liquor, the di-potassium salt (yellow in colour), of the 4-sulpho-3 : 5-dinitrosalicylic acid, crystallised. The yields of the 4-sulpho-3 : 5-dinitrosalicylic acid and its di-potassium salt were small. (Found: Equivalent, 317·7; K, 12·0; H_2O, 5·5; $C_7H_4O_8NSK$, H_2O, requires equivalent, 319·2; K, 12·2; H_2O, 5·6 per cent.)

Neutral barium-4-sulpho-5-nitrosalicylate.—The above potassium salt was neutralised and converted into the barium salt, which is difficultly soluble in boiling water and crystallised from it in orange coloured plates, with a molecule of water, which is not removed even on heating at 200° under reduced pressure. (Found: Ba, 32·9; $C_7H_3O_8NSBa$, H_2O requires Ba, 33·0 per cent.)

4-Sulpho-5-nitro-salicylic acid was obtained as usual from the above barium salt. It is hygroscopic. It crystallised from water in pale yellow needles, with two molecules of water. It was dried over calcium chloride and then analysed; m.p. 166-167°. (Found: Equivalent, 148·2; N, 4·6; S, 10·7; H_2O, 11·8; $C_7H_5O_8NS$, $2H_2O$ requires equivalent, 149·6; N, 4·7; S, 10·7; H_2O, 12·0 per cent.)

4-*Sulpho*-3 : 5-*dinitro-salicylic acid*.—Besides a small quantity obtained above while preparing 4-sulpho-5-nitrosalicylic acid, it was obtained in good yield by employing the same proportions but allowing the temperature to rise freely, which is helped by the considerable evolution of heat, during addition of nitric acid. On cooling it separated as a solid which crystallised from water in pale yellow needles or scales, decomposing above 261°. A further yield is obtained as the di-potassium salt by pouring the mother liquor into potassium chloride solution. (Found : S, 10·6 ; N, 9·3 ; $C_7H_4O_{10}N_2S$ requires S, 10·4 ; N, 9·1 per cent.)

Di-potassium-4-*sulpho*-3 : 5-*dinitro-salicylate* obtained as above crystallised from water in tiny yellow scales. (Found : K, 20·4 ; S, 8·4 ; $C_7H_2O_{10}N_2SK_2$ requires K, 20·3 ; S, 8·3 per cent.).

Monopotassium-4-*sulpho*-3:5-*dinitro-salicylate* was obtained by acidifying the above salt with hydrochloric acid. It crystallised from water as tiny microscopic needles, yellow in colour. (Found : K, 11·3 ; $C_7H_3O_{10}N_2SK$ requires K, 11·3 per cent.)

Neutral barium-4-*sulpho*-3 : 5-*dinitro-salicylate* was obtained by neutralising the acid with barium carbonate. It is more soluble in water than the corresponding salt of the mononitro acid and crystallised from it in red needles, with two molecules of water, which cannot be removed even after heating under reduced pressure. (Found : Ba, 28·3 ; $C_7H_2O_{10}N_2SBa$, $2H_2O$ requires Ba, 28·6 per cent.)

2 : 4 : 6-*Trinitro-phenol-m-sulphonic acid* was obtained by heating the 4-sulphosalicylic acid (desiccated, 10 g.) with concentrated nitric acid (sp. gr. 1·4 ; 15 c.c.) at 100° for an hour. Excess of nitric acid was then evaporated at 100°. The solid obtained crystallised from water in pale yellow cubes, with four molecules of water of crystallisation, m.p. 105°. It is hygroscopic. (Found : N, 11·0 ; S, 8·2 ; H_2O, 18·3 ; $C_6H_3O_{10}N_3S$, $4H_2O$ requires N, 11·0 ; S, 8·4 ; H_2O, 18·9 per cent.)

5-*Amino*-4-*sulphosalicylic acid*.—To 5-nitro-4-sulphosalicylic acid (5 g.) dissolved in alcohol, ammonium sulphide (5 N ; 30 c.c.) was added and the mixture refluxed for two hours. Having filtered off the sulphur, the mother liquor gave a solid on concentration. It is difficultly soluble in water from which it crystallised as yellowish thin scales, decomposing above 260°. Yield, 4 g. (Found : S, 13·6 ; N, 6·1 ; $C_7H_7O_6NS$ requires S, 13·8 ; N, 6·0 per cent.)

3-*Nitro*-5-*amino*-4-*sulpho-salicylic acid*. To 3 : 5-dinitro-4-sulphosalicylic acid (5 g.) dissolved in alcohol, ammonium sulphide (5 N, 50 c.c.) was added and the mixture heated as above. A solid (3·8 g.) difficultly soluble

in water, from which it crystallised in long yellow needles, was obtained, decomposing above 280°. (Found: S, 11·3; N, 9·9; $C_7H_6O_8N_2S$ requires S, 11·5; N, 10·1 per cent.)

3: 5-*Diamino*-4-*sulphosalicylic acid*.—3: 5-dinitro-4-sulphosalicyclic acid (2 g.) was dissolved in hydrochloric acid and reduced with iron. The solid separating is sparingly soluble in water, from which it crystallised as rectangular dark coloured cubes, decomposing above 290°. (Found: S, 12·8; N, 11·4; $C_7H_8O_6N_2S$ requires S, 12·9; N, 11·3 per cent.)

The authors are grateful to Dr. T. S. Wheeler for his great interest in the work.

Summary.

It is shown that the sulphonic acid group outside the directing influences of the -OH and -COOH groups cannot be substituted by the nitro group as in 3-, or 5-sulphosalicylic acids.

Thus on nitration of 4-sulphosalicylic acid, (I) 4-sulpho-5-nitro-salicylic acid, (II) 4-sulpho-3: 5-dinitrosalicylic acid, and (III) 2: 4: 6-trinitrophenol-*m*-sulphonic acid were obtained.

REFERENCES.

1. Datta and Varma, *J. Amer. Chem. Soc.*, 1919, **41**, 2039.
2. Meldrum and Hirwe, *J. Ind. Chem. Soc.*, 1930, **7**, 888.
3. Berndsen, *Annalen*, 1875, **177**, 97.
4. Hirwe and Jambhekar, *J. Ind. Chem. Soc.*, 1933, **10**, 47–51.

STUDIES ON THE ANISOTROPY OF THE OPTICAL POLARISATION FIELD IN LIQUIDS.—PART I.

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(Communicated by Mr. S. Bhagavantam.)

1. Introduction.

Extensive investigations by Raman and Krishnan (1928) relating to the electric, optical and magnetic behaviour of liquids have shown that the optical polarisation field surrounding a liquid molecule should, in general, be regarded as anisotropic. A marked diminution in the effective optical anisotropy of certain molecules and a conspicuous failure of the well-known Lorentz formula for the refractivity of certain compounds as we pass from the vapour to the liquid state are usually regarded as typical examples of the experimental facts which receive a satisfactory explanation on this basis. It must, however, be mentioned that the above two tests involve respectively an accurate knowledge of the depolarisation of the scattered light and the refractive index of the substance under question in the vapour state. Recent investigations (Ananthakrishnan, 1935 and H. Volkmann, 1935) have cast some doubt on the reliability of the older results regarding the depolarisation measurements, especially when the values are small, as in the case of gases and vapours; and undisputed values of the refractive indices are available, if at all, only for a few vapours.

A different line of attack would, however, consist in examining the applicability or otherwise of the Lorentz law within the liquid phase itself by altering the temperature. Such a procedure would require an accurate knowledge only of the refractive index and the density of the liquids under investigation at different temperatures, both of which could be obtained with a reasonable certainty. Although reliable data are available for the dependence of density on temperature in many liquids, the variation in refractive index with temperature is known only in a few cases; and even in such cases only over very narrow ranges of temperature. Working on these meagre data alone, Raman and Krishnan (1928) and later Krishnan (1930) have shown that they indicate a break-down of the Lorentz law. In view of the very narrow range in which this aspect of the question has been

examined, it is felt that the majority of evidence available to-day in support of the anisotropic nature of the optical polarisation field depends on the reliability of the measurements of depolarisation of the scattered light and the index of refraction in vapours. Hence, in the present paper extensive data regarding the temperature variation of refractive index for a large number of typical liquids are obtained and, as the variation of density with temperature is already known with sufficient accuracy in these cases, the results are expected to throw light on the validity or otherwise of the Lorentz law without having recourse to the more difficult measurements of the depolarisation of the scattered light and the refractive index of the vapour. The liquids examined here are carbon disulphide, benzene, hexane and carbon tetrachloride. The choice is based on various considerations, such as the varying degrees of optical anisotropy and it is well known that the series constitute a typical set of molecules of special interest from the point of view of light-scattering.

2. *Experimental.*

An Abbe Refractometer is used in measuring the refractive indices of liquids at different temperatures. The refractometer is first standardized by means of the glass test-piece provided with the instrument. The refractometer prisms are then connected with a copper spiral, through which a steady flow of water is maintained with the help of a constant-pressure arrangement. The spiral can be either immersed in cold water or heated by an instantaneous water-heater for low or high temperature work. The instrument is provided with a thermometer reading from 5–70° and refractive index measurements can be made at all intermediate temperatures.

The following tables give the observed refractive indices, densities taken from *I. C. T.* and the molecular refractivities calculated therefrom at different temperatures in the cases of carbon disulphide, benzene, hexane and carbon tetrachloride. The liquids have been purified by distillation at constant boiling point before use.

TABLE I.

Carbon disulphide.

Temp.	10	15	20	25	30	35	40	45
Ref. index	1·6360	1·6320	1·6280	1·6240	1·6196	1·6152	1·6108	1·6065
Density	1·2780	1·2705	1·2629	1·2554	1·2479	1·2403	1·2328	1·2252
Mol. Refractivity ..	21·355	21·373	21·393	21·411	21·418	21·426	21·432	21·443

TABLE II.

Benzene.

Temp.	15	20	25	30	35	40	45	50	55	60
Ref. index ..	1·5042	1·5012	1·4980	1·4950	1·4920	1·4884	1·4850	1·4820	1·4782	1·4752
Density ..	0·8841	0·8788	0·8734	0·8681	0·8628	0·8575	0·8521	0·8468	0·8414	0·8361
Mol. Refractivity	26·157	26·184	26·204	26·229	26·254	26·256	26·262	26·286	26·288	26·301

TABLE III.

Hexane.

Temp.	15	20	25	30	35	40	45	50	55	60	65
Ref. index ..	1·3790	1·3760	1·3732	1·3705	1·3680	1·3652	1·3625	1·3595	1·3568	1·3540	1·3510
Density	0·6643	0·6596	0·6552	0·6505	0·6459	0·6412	0·6365	0·6318	0·6270	0·6221	0·6172
Mol. Refractivity	29·965	29·966	29·975	29·988	30·019	30·032	30·054	30·052	30·078	30·100	30·108

TABLE IV.

Carbon tetrachloride.

Temp.	20	25	30	35	40	45
Ref. index	1·4610	1·4578	1·4546	1·4513	1·4480	1·4450
Density	1·5941	1·5846	1·5749	1·5652	1·5557	1·5461
Mol. Refractivity	26·480	26·482	26·481	26·477	26·480	26·480

3. *Discussion of Results.*

The pronounced temperature variation in the molecular refractivity of CS_2, C_6H_6, C_6H_{14} may easily be seen from the tables and from the curves given in Fig. 1. This result definitely shows that the assumption of an isotropic optical polarisation field which forms the basis of the Lorentz law is unjustifiable in some liquids. On the other hand, in the case of carbon tetrachloride the molecular refractivity is more or less constant and it may therefore be concluded that in this liquid, the optical polarisation field is isotropic. Such a conclusion is in agreement with the structure and a number of other experimental facts regarding this molecule. The derivation of the constants of anisotropy of the optical polarisation field and the significance

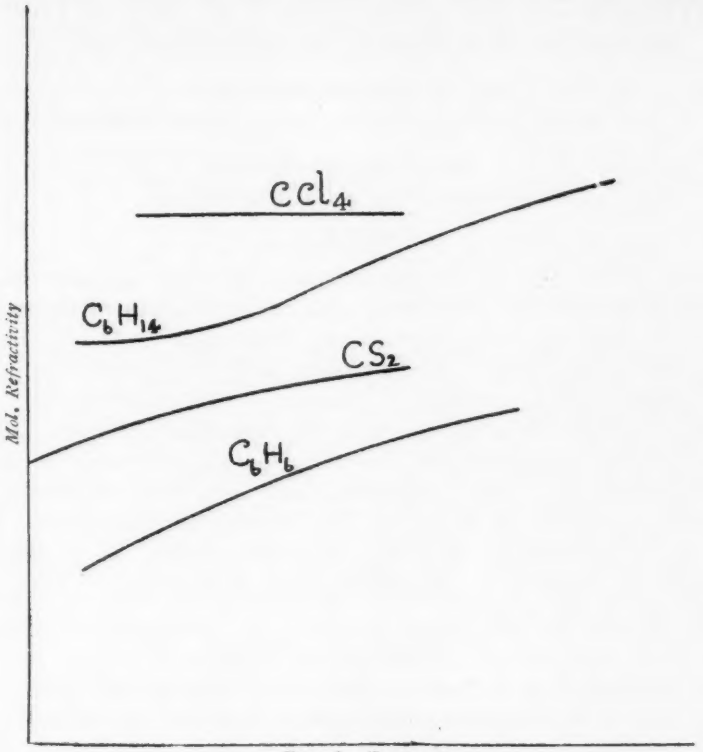

FIG. 1.—Temperature

of such constants to the subject of light-scattering will form the subject-matter of Part II.

4. *Summary.*

The molecular refractivity is found to increase with temperature in CS_2, C_6H_6 and C_6H_{14} liquids. On the other hand, in CCl_4, it remains constant. These results indicate that the optical polarisation field is anisotropic in the former three liquids whereas it is isotropic in the case of CCl_4.

REFERENCES.

R. Ananthakrishnan, *Proc. Ind. Acad. Sci.*, 1935, **2**, 153.

K. S. Krishnan, *Proc. Roy. Soc.*, 1930, **126A**, 155.

C. V. Raman and K. S. Krishnan, *Proc. Roy. Soc.*, 1928, **117**, 1, 589.

C. V. Raman and K. S. Krishnan, *Phil. Mag.*, 1928, **5**, 498.

H. Volkmann, *Ann. Der Phys.*, 1935, **24**, 457.

STUDIES ON THE ANISOTROPY OF THE OPTICAL POLARISATION FIELD IN LIQUIDS.—PART II.

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Received February 22, 1936.
(Communicated by Mr. S. Bhagavantam.)

1. *Introduction.*

In Part I of this series, the molecular refractivity of certain liquids has been determined at different temperatures. The results supported the view that the optical polarisation field surrounding a liquid molecule should, in general, be regarded as anisotropic. In the present paper, it is proposed to calculate the constants, which constitute a measure of such an anisotropy. These constants, along with a knowledge of the compressibilities, etc., may be utilised for determining the depolarisation of the light scattered by the liquid under investigation. Such calculations have been extended to the entire range of temperatures at which data have been gathered in Part I. In this way, we are enabled to study the dependence firstly, of the anisotropic constants and secondly, of the depolarisation of the scattered light, on the temperature of the liquid.

2. *Method of Calculation.*

As will be noticed from Part I, the choice of liquids has been restricted to such cases in which the molecules possess an axis of symmetry. If A, C and C represent the principal optic moments for a vapour molecule and p_1, p_2 and p_2 the corresponding constants characteristic of the optical polarisation field surrounding the molecule in the liquid state, we have the following relationships :—

$$n_v - 1 = 2\pi v_v \frac{A + 2C}{3} \quad .. \quad .. \quad .. \quad .. \quad (1)$$

$$\frac{10\, r_v}{6 - 7r_v} = 2\left(\frac{A - C}{A + 2C}\right)^2 \quad .. \quad .. \quad .. \quad .. \quad (2)$$

$$Ap_1 + 2Cp_2 = \frac{3}{v_l} - \frac{4\pi\,(A + 2C)}{n_l^2 - 1} \quad .. \quad .. \quad .. \quad (3)$$

$$p_1 + 2p_2 = 4\pi \quad .. \quad .. \quad .. \quad .. \quad .. \quad (4)$$

n_v, v_v and r_v represent respectively the refractive index, number of molecules per c.c. and the depolarisation of the transversely scattered light in the vapour state. A knowledge of these quantities will enable us to calculate A and C for the various molecules from equations (1) and (2). Substituting these in equations (3) and (4), we obtain the values of p_1 and p_2 after replacing v_l

and n_l, the number of molecules per c.c. and the refractive index respectively in the liquid state by the observed values. The constants of the anisotropic polarisation field so derived may be made use of in calculating the depolarisation of the transversely scattered light in the liquid state with the help of the following formula :

$$r_l = \frac{2\nu_l F}{kT\beta\left(\frac{n_l^2-1}{4\pi}\right)^2 + \frac{7}{3}\nu_l F}$$

where

$$F = \tfrac{1}{15}(A' - C')^2 ; \; A' = A\left(1 + p_1 \frac{n_l^2 - 1}{4\pi}\right), \text{ etc.}$$

It may be noted that by making $p_1 = p_2 = \frac{4\pi}{3}$, all the above formulæ reduce to the usual expressions characteristic of the isotropic optical polarisation field. The derivation of the above equations is contained in a large number of papers dealing with the subject of light-scattering (Raman and Krishnan, 1928) and hence will not be repeated here. By repeating this process for each one of the temperatures, we obtain values for the constants p_1 and p_2 and for r_l the depolarisation of the light scattered by the liquid at different temperatures. The latter have also been determined experimentally at some convenient temperatures in the present investigation. In the following tables θ represents the temperature on the centigrade scale and β the compressibility. p_1 and p_2, the constants of the polarisation field, have been given to three places of decimals only for purposes of calculation and to bring out the trend of variation in them more prominently. Their absolute values are not significant to such an extent.

3. *Results.*

TABLE I.

Carbon disulphide.

$C = 5{\cdot}892 \times 10^{-24}$; $A = 14{\cdot}426 \times 10^{-24}$; $(n_v - 1) \times 10^6 = 1485$; $r_v = 0{\cdot}111$.

θ	10	15	20	25	30	35	40	45
n_l ..	1·6360	1·6320	1·6280	1·6240	1·6196	1·6152	1·6108	1·6065
p_1 ..	2·866	2·866	2·900	2·926	2·926	2·936	2·936	2·936
p_2 ..	4·852	4·852	4·835	4·822	4·822	4·817	4·817	4·817
p_2/p_1 ..	1·692	1·692	1·667	1·647	1·647	1·640	1·640	1·640
$\beta \times 10^{12}$ ..	..	..	92·7	..	100·0	..	..	..
$100r_l$ calc. ..	..	..	61·8	..	60·3	..	..	..
$100r_l$ obs. ..	..	..	65·3	..	63·5	..	..	..

TABLE II.

Benzene.

$C = 12{\cdot}828 \times 10^{-24}$; $A = 6{\cdot}475 \times 10^{-24}$; $(n_v - 1) \times 10^6 = 1820$; $r_v = 0.0445$.

θ	15	20	25	30	35	40	45	50	55	60
n_t ..	1·5042	1·5012	1·4980	1·4950	1·4920	1·4884	1·4850	1·4820	1·4782	1·4752
p_1 ..	6·940	6·866	6·784	6·764	6·742	6·736	6·705	6·662	6·658	6·642
p_2 ..	2·815	2·852	2·893	2·903	2·914	2·917	2·933	2·954	2·956	2·964
p_1/p_2	2·465	2·407	2·344	2·330	2·313	2·309	2·286	2·255	2·252	2·240
$\beta \times 10^{12}$	90·75	94·50	98·25	102·00	106·00	110·00	114·50	119·00	123·50	128·00
$100r_l$ calc.	40·2	39·9	39·7	39·0	38·2	37·4	37·3	36·3	35·5	34·8
$100r_l$ obs.	42·8	..	..	40·6	..	..	..	..	..	36·7

TABLE III.

Hexane.

$C = 10{\cdot}694 \times 10^{-24}$; $A = 14{\cdot}473 \times 10^{-24}$; $(n_v - 1) \times 10^6 = 2032$; $r_v = 0{\cdot}115$.

θ	15	20	25	30	35	40	45	50	55	60	65
n_l ..	1·3790	1·3760	1·3732	1·3705	1·3680	1·3652	1·3625	1·3595	1·3568	1·3540	1.3510
p_1 ..	1·998	1·985	1·971	2·083	2·252	2·315	2·432	2·408	2·548	2·673	2·707
p_2 ..	5·286	5·293	5·299	5·244	5·159	5·128	5·069	5·081	5·011	4·949	4·932
p_2/p_1 ..	2·646	2·666	2·688	2·518	2·290	2·215	2·084	2·110	1·966	1·851	1·821
$\beta \times 10^{12}$ ..	..	157	..	..	..	..	..	206	..	..	..
$100r_l$ calc. ..	..	7·5	..	..	..	..	..	7·8	..	..	..
$100r_l$ obs. ..	..	9·4	..	..	..	..	..	8·2	..	..	..

4. Discussion of Results.

(*a*) *Carbon disulphide, benzene and hexane.*—As has already been pointed out, the polarisation field in these three substances is to be regarded as anisotropic contrary to the case of CCl_4. These substances are therefore dealt with here and CCl_4 will be considered separately in a subsequent paragraph. Tables I, II and III show that the ratio p_1/p_2 in the case of benzene and p_2/p_1 in the cases of CS_2 and C_6H_{14} tends to diminish with increasing temperature. This indicates that with increasing temperature the polarisation field is becoming more and more isotropic as may be expected. Similar results have

been obtained by Krishnan and Ramachandra Rao (1929) from a consideration of the variation of depolarisation of scattered light with temperature. Hexane has been studied by these authors and the results obtained in this investigation are in fair agreement with those reported earlier by them. It may be mentioned here that benzene, carbon disulphide and hexane are typical examples in which the light scattering experiments (Ramachandra Rao, 1927) show that the optical anisotropy increases with increasing temperature. This result is consistent with the observed approach of the ratio p_1/p_2 to unity and a consequent increase in the molecular refractivity with increasing temperature. On the contrary, liquids are known, in which the effective optical anisotropy decreases with increasing temperature and in such cases deviations from the Lorentz law of an opposite type should be expected. Examples of this kind are some of the fatty acids which are characterised by a marked degree of association. These liquids are under investigation and the results will form the subject-matter of a further communication.

(*b*) *Carbon tetrachloride.*—It will be noticed from the results given in Part I that the molecular refractivity of this substance is more or less constant with temperature. This means that the polarisation field surrounding the CCl_4 molecules is isotropic. Such a conclusion is in perfect agreement with the tetrahedral structure of the molecule. This view has an important consequence regarding the depolarisation of the scattered light in the vapour state and its relation to that observed in the liquid state. In the case of an isotropic polarisation field the formula connecting the two may be given as

$$\frac{RT\beta}{N}\,\nu_l\,\frac{r_l}{6-7r_l}=\frac{r_v}{6-7r_v}.$$

Taking the depolarisation of the liquid as 0·04 and the compressibility as 105×10^{-12}, the value of r_v may be calculated to be 0·0011. This result is in marked disagreement with the hitherto accepted values for the depolarisation of the light scattered by CCl_4 vapour, thus definitely not supporting the idea of a perfectly isotropic polarisation field in CCl_4. On the other hand, more recent measurements of Ananthakrishnan (1935) show that the upper limit for the depolarisation in this case is only 0·0015. This figure is in excellent agreement with the calculated value and supports strongly the view that the optical polarisation field is isotropic. If the polarisation field is isotropic, one would expect the molecule also to be optically isotropic and hence the origin of this small depolarisation remains a mystery. It may perhaps be attributed to the isotopic molecules or to the admixture of depolarised Raman radiations as has been done by other investigators on previous occasions.

5. Summary.

From a knowledge of the molecular refractivities at different temperatures, the anisotropic constants of the optical polarisation field are calculated in CS_2, C_6H_6 and C_6H_{14}. It is found that the polarisation field becomes more and more isotropic with increasing temperature.

From these constants, the dependence on temperature of the depolarisation of scattered light in these liquids is also deduced. Experimental observations, made at some convenient temperatures, are compared with the calculations.

Evidence in support of the view that the optical polarisation field in CCl_4 is isotropic is presented.

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REFERENCES.

R. Ananthakrishnan, *Proc. Ind. Acad. Sci.*, 1935, **2**, 153.

K. S. Krishnan and S. Ramachandra Rao, *Ind. Jour. Phys.*, 1929, **4**, 39.

C. V. Raman and K. S. Krishnan, *Phil. Mag.*, 1928, **5**, 498.

S. Ramachandra Rao, *Ind. Jour. Phys.*, 1929, **3**, 1, 21.

THE ALKALOIDS OF HOLARRHENA ANTI-DYSENTERICA.

Part IV. The Occurrence of Two Further New Bases in the Bark of Indian Holarrhena and their Relationship to Conessine and Holarrhimine.

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THERE are six different bases theoretically possible according to the number and position of the methyl groups attached to the two nitrogen atoms in the conessine nucleus, $C_{21}H_{31}N_2\geqslant$. Of these the di-tertiary base, conessine, occurs in the Indian Holarrhena bark to the extent of about 0·4 per cent. The bases, conessimine,[1] iso-conessimine and conimine,[2] isolated later from the bark and the seeds of the plant in about one-tenth of the yield of conessine, proved to be the nor-bases of conessine answering respectively to the formulæ II, III, and IV, as appeared probable through their methylation to conessine[3] and was later definitely established by the N-demethylation of conessine to iso-conessimine and conimine, with the help of BrCN.[4]

$C_{21}H_{31}$: NMe . $N(Me)_2$ (I) $\quad$ $C_{21}H_{31}$: NH . $N(Me)_2$ (II) $\quad$ $C_{21}H_{31}$: NMe . NH(Me) (III) $\quad$ $C_{21}H_{31}$: NH . NH(Me) (IV)

$C_{21}H_{31}$: NMe . NH_2 (V) $\quad$ $C_{21}H_{31}$: NH . NH_2 (VI)

It appeared interesting to investigate at this stage, if the two remaining bases, V and VI, were also present in the plant, and if they could, by a suitable method of further demethylation, be directly obtained from it. The isolation or synthesis of the completely demethylated base VI was of particular interest owing to its apparently simple relationship to the oxygenous base holarrhimine, $C_{21}H_{36}ON_2$,[5] whose molecular formula differed from it by one H_2O.

Attempts to synthesise the two bases have not yet fructified. It has, however, been possible to isolate from the mother liquors of holarrhimine

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1 *J. Ind. Chem. Soc.*, 1932, **9**, 553.
2 *Ibid.*, 1934, **11**, 283.
3 Ref. 2.
4 *Ibid.*, 1934, **11**, 787.
5 Ref. 1.

sulphate two bases whose hydrochlorides were fairly soluble in water but insoluble in 10 per cent. HCl, and which appear, partly on indirect evidence, to conform to the formulæ V and VI. These two bases which the author proposes to name as conamine and conarrhimine, taking into consideration their apparent relationship to conimine and holarrhimine respectively, were separated from each other by fractional crystallisation from petroleum ether in which conamine is more easily soluble than conarrhimine. The former, however, was too little in quantity to admit of a detailed study and the latter, conarrhimine, could not be obtained free from holarrhimine, into which it is slowly converted in the process of purification through absorption of moisture during repeated crystallisation from hot solvents.

$$\underset{\text{Conarrhimine}}{C_{21}H_{31}\begin{matrix}.NH_2\\:NH\end{matrix}} + H_2O = \underset{\text{Holarrhimine}}{C_{21}H_{31}\begin{matrix}.NH_2\\.NH_2\\.OH\end{matrix}}$$

In the course of this work, the author was forced to the conclusion that conarrhimine and holarrhimine form eutectic mixtures melting sharply, like any other bases of this series, at 160° and 175°. The study of these two mixtures which are both completely converted into holarrhimine on heating in moist ethyl acetate solution on the water-bath, explains the isolation of kurchicine by Ghosh[6] and later by Bertho and co-workers.[7]* But although attempts to isolate pure conarrhimine have failed, its reaction product with nitrous acid, which was got in sufficiently pure condition for analysis, establishes its presence in the plant. In fact it is holarrhimine whose natural occurrence becomes doubtful in the face of the above observations, but the ease with which conarrhimine is converted into holarrhimine makes it very probable that both these bases are originally present in the Holarrhena bark.

The five active hydrogen atoms in the above formula for holarrhimine were established by the formation of tetra-N-methyl holarrhimine and subsequent acetylation and benzoylation of its hydroxyl group. The diprimary character of holarrhimine was also indicated by its reaction with nitrous acid, whereby a nitrogen-free substance (described in a separate communication was obtained, contrary to the suggestion contained in Part I[8] (Siddiqui and Pillay, *loc. cit.*) that the non-basic oily product obtained in this reaction

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[6] *Ibid.*, 1928, **5**, 477.

[7] *Ber.*, 1933, **66**, 786.

* The latter authors' conkurchicine ($C_{20}H_{32}N_2$) m.p. 153° may also prove on further investigation in the light of these findings to be perhaps a more uniform sample of conarrhimine, while their conessidine ($C_{21}H_{32}N_2$) m.p. 123°, may eventually prove to correspond to one of the two mono methyl bases conamine and conimine ($C_{22}H_{36}N_2$), melting at 130° and 134° respectively.

[8] Ref. 1.

could be a nixture of mono- and di-nitroso derivatives which failed to crystallise on that account and was not tested any farther. The same authors had also noted only 3 as against 5 active hydrogens in holarrhimine. In view, however, of the experimental evidence above and a fresh corroboration of the earlier finding in respect of the active H determination after Zerewitinoff, the negative error in the active H values has to be explained as being very probably due to the fact that on mixing the magnesium methyl compound in amyl ether solution with the pyridine solution of holarrhimine the latter is partly thrown out of the reaction medium owing to its sparing solubility in amylether.

It may thus be concluded from the foregoing observations, that conarrhimine forms the mother base of the alkaloidal constituents of holarrhena antidysenterica, through direct step-wise methylation on the one hand, and on the other through the hydrolysis of its nitrogen ring to holarrhimine, which may very possibly be the starting point of another series of methylation products, whose occurrence in the bark becomes quite plausible in view of the finding that the yield of tetra-N-methyl holarrhimine from the direct methylation of the total alkaloids is far in excess of the yield of holarrhimine in the same sample of the bark (*vide* experimental). Holarrhimine also may be the source of several oxidation and degradation products, which the author has reason to suspect in the bark but which have not so far been obtained sufficiently pure for communication. One such degradation product may be "lettocine" $C_{17}H_{25}O_2N$, lately reported by Peacock and Chaudhri[9] but in so far as the holarrhena bases invariably crystallise in well-defined forms and are colourless in state of final purity, lettocine also, which is reported as a "light brown, microcrystalline powder," cannot be considered sufficiently pure to give a dependable molecular formula. Discussing these possibilities, it may also be stated here, that the isomerisation of conessine and its norbases[10] made the author suspect the presence of the iso-bases in the Holarrhena bark, but a long and careful search for them in the total alkaloids from 30 Kg. of bark has forced a contrary conclusion.

Experimental.

Isolation of the bases.—From the mother liquors of the insoluble holarrhimine sulphate described in Part I (*loc. cit.*) a fraction of petroleum ether insoluble hydrates was obtained which yielded about 10 gms. of a hydrochloride, soluble in water and insoluble in 10 per cent. HCl. After repeated fractional crystallisation from petroleum ether, with addition of very little

[9] *J. C. S.*, 1935, 734.

[10] *Proc. Ind. Acad. Sci.*, 1935, **2**, 426.

quantities of ethyl acetate, conamine, finally melting at 130° and giving a depression of 15° with conimine was obtained from the more soluble end fraction. (Yield: 1 g., 0·3 per cent. of total alkaloids.) The less soluble fraction yielded, after repeated alternate crystallisations from acetone and ethyl acetate, a white crystalline base melting at 158–60°. (Yield: 3 g., 1 per cent. of the total alkaloids.)

The residue from the mother liquors of holarrhimine (Part I, *loc.cit.*) melted slowly at 140–65.° This yielded through repeated fractional crystallisation from ethyl acetate and acetone after its initial exhaustion withpetroleum ether, a base melting at 173–75°, and apparently corresponding to kurchicine.

Conamine—$C_{22}H_{36}N_2$, crystallises from petroleum ether, acetone, and ethyl acetate in clusters of slender needles, m.p. 130°. It is fairly soluble in all the organic solvents, less so in petroleum ether. In 1 per cent. absolute alcoholic solution it showed $[\alpha]_D^{28°} = -19°$ as against $-30°$ noted for conimine. (Found: C, 79·90, 79·85; H, 11·4, 11·3; N, 7·8; N—CH_3, 4·4; $C_{22}H_{36}N_2$ requires C, 80·5; H, 11·0; N, 8·5; CH_3 for 1 N—CH_3, 4·6 per cent.) It forms a water soluble and 10 per cent HCl insoluble white, crystalline hydrochloride and also other salts, but a full characterisation of the base and the salts had to be postponed for the present owing to lack of sufficient quantity. A further differentiation between conamine and conimine was, however, established through the fact that on heating in moist ethyl acetate to dryness on the water-bath, conimine remained unchanged while conamine was converted into a high melting product (m.p. 220–40°) which could not be sufficiently purified or studied owing to lack of enough quantity but which may bear a similar relationship to conamine as holarrhimine does to conarrhimine.

The eutectic mixtures of conarrhimine and holarrhimine.—The base melting at 159-60° crystallises in clusters of white, well-defined needles from acetone and ethyl acetate in which it is distinctly more soluble than holarrhimine. In 1 per cent. absolute alcoholic solution it showed $[\alpha]_D^{35°} = -20°$ as against $[\alpha]_D^{35°} = -11°$ for holarrhimine and $[\alpha]_D^{35°} = -10°$ noted for 173-75° base in parallel observations. In 1 per cent. chloroform solution the 159-60° base showed $[\alpha]_D^{34°} = -29°$ as against $[\alpha]_D^{25°} = -14°$ for holarrhimine reported in Part I (*loc. cit.*). After drying to constant weight over phosphorous pentoxide at 100° *in vacuo* (Found: C, 77·26, 77·32; H, 10·94, 11·15; N, 7·46; $C_{21}H_{34}N_2$ requires C, 80·3; H, 10·8; N, 8·9 ($C_{21}H_{36}ON_2$ requires C, 76·7; H, 11·0; N, 8·1; a mixture of 2 parts $C_{21}H_{36}ON_2$ and 1 part $C_{21}H_{34}N_2$ requires C, 77·9; H, 10·9; and N, 8·3 per cent.). The base melting at 160° thus appears to be a mixture of about 2 parts of holarrhimine and 1 part of conarrhimine.

On repeatedly heating the 160° base (1 g.) in ethyl acetate solution over a layer of water to dryness on the water-bath, the residue which was very slightly coloured, melted at 180°-82°, gave no depression with holarrhimine, melting at 182-83°, and showed within limits of error the same rotation as holarrhimine. After drying to constant weight at 100° *in vacuo* (Found: C, 75·3; H, 10·9; N, 8·0; holarrhimine, $C_{21}H_{36}ON_2$ requires C, 75·9; H, 10·8; N, 8·4. Before heating with water the 160° base gave C, 77·32; H, 11·15; N, 7·46 per cent.). The base melting at 173-75° also gave holarrhimine on heating with ethyl acetate and water as described above, the identity in this case being fixed through the mixed melting point and optical activity.

The salts of the 160° base crystallise in well-defined forms, the Pt value of the platinate corresponding to the value theoretically required.

Reaction product of conarrhimine and nitrous acid.—Nitroso-oxyapo-conarrhimine.—To test the presence of conarrhimine in the combined mother liquors of conamine at 160° base the residue from these mother liquors was treated in acetic acid solution with excess of sodium nitrite, and the reaction mixture shaken out with ethyl acetate, whereby the basic reaction product of conamine $C_{21}H_{31}\begin{matrix}-\ NH_2\\ >\ NCH_3\end{matrix}$ and nitrous acid: $C_{21}H_{31}OH:NCH_3$ remained in the aqueous acidic layer. The ethyl acetate containing the non-nitrogenous product, $C_{21}H_{31}(OH)_3$ (discussed in a later communication) from holarrhimine $C_{21}H_{31}OH\begin{matrix}:NH_2\\ .NH_2\end{matrix}$ and the mono nitroso non-basic derivative $C_{21}H_{31}\begin{matrix}:N.NO\\ .OH\end{matrix}$ from conarrhimine $C_{21}H_{31}\begin{matrix}-\ NH_2,\\ >\ NH\end{matrix}$ for which the name nitroso-oxy-apo-conarrhimine is suggested, was washed with water and alkali, dried and freed of the solvent. The residue was taken up in dry petroleum ether, which kept holarrhol in solution and yielded the nitroso product as a slightly coloured, crystalline powder, which stuck to the sides at 145° and melted giving a miniscus at 160-63° (Found: C, 73·46; H, 9·63; N, 7·43; $C_{21}H_{31}\begin{matrix}:N.NO\\ .OH\end{matrix}$ requires C, 73·25, H, 9·30; N, 8·13 per cent.). Nitroso-oxy-apo-conarrhimine is sparingly soluble in petroleum ether, fairly soluble in all the other organic solvents and insoluble in water or dilute acids or alkalies.

Methylation of Holarrhimine: *Tetra-N methyl holarrhimine.*—1 g. holarrhimine was refluxed at 100° with 6 mols. each of formaldehyde (40%) and formic acid for about an hour, till no more carbon dioxide evolved. The pale yellow treacly reaction product was dissolved in water and treated with sodium sulphate solution to remove the very sparingly soluble sulphate of

any unchanged holarrhimine, but no precipitate was formed. The base was then liberated with caustic soda solution and taken up in acetic ether. On drying over sodium sulphate, removing the solvent and cooling the hot alcoholic solution of the residue, tetra N-methyl holarrhimine crystallised in colourless prismatic rods, melting at 233-35° (yield 0·9 g. 85 per cent. of theory).

Also on direct methylation of total alkaloids from 2 kg. Holarrhena bark with excess of formaldehyde and formic acid and working up the petroleum ether insoluble portion of the resultant product, tetra N-methyl holarrhimine was obtained in a fairly large yield (about 0·15 per cent. on the weight of the bark while the yield of holarrhimine in the same sample was noted as 0·05 per cent.).

Characterisation of Tetra N-methyl Holarrhimine and its Derivatives.—

Tetra N-methyl holarrhimine, $C_{25}H_{44}ON_2$ (Plate XVII) m.p. 233-35° is readily soluble in chloroform, fairly soluble in hot ethyl alcohol and methyl alcohol, less so in the cold, difficultly soluble in benzene, acetone and ethyl acetate, nearly insoluble in ether and petroleum ether. It showed in 1 per cent. absolute alcoholic solution $[\alpha]_D^{33°} = -45·5°$. In sulphuric acid conc. it dissolves to a colourless solution on warming and slowly developes a reddish orange colour which fades on addition of water. (Found : C, 77·4, 77·2 ; H, 11·2, 11·2 ; N, 7·2 ; N—CH_3 after Herzig and Meyer 15·7 ; $C_{25}H_{44}ON_2$ requires C, 77·3 ; H, 11·3 ; N, 7·2 ; CH_3 for 4 N-methyls 15·5 per cent.).

—*hydrochloride* came out on adding together the components in ethereal solution in aggregates of colourless short needles, easily soluble in alcohol and water, insoluble in acetone and ether, and melting with frothing at 315-16°.

—*hydroiodide.*—On adding KI solution to an acetic acid solution of the base the hydroiodide directly crystallised out in bundles of feather-like aggregates of short, tapering prismatic rods sparingly soluble in water and alcohol in the cold, fairly soluble in the hot and melting with frothing at 302-3°.

—*hydrobromide,* prepared similarly as the hydroiodide, came out in short scattered needles, sparingly soluble in alcohol, a little more soluble in water than the hydroiodide and melting at 306-7°.

—*picrate,* was obtained by adding aqueous picric acid to the aqueous solution of the hydrochloride and crystallising the precipitate from hot water, when it formed a bright yellow crystalline powder. It is fairly soluble in hot alcohol, very sparingly in hot water, sticks to the sides at 225° and melts at 272-75°.

—*chloroplatinate* came out on adding 10 per cent. platinic chloride to an aqueous solution of the hydrochloride, as an amber coloured granular

precipitate which crystallised on keeping, in aggregates of prismatic rods m.p. 251-52° (Found: 24.46; $C_{25}H_{44}ON_2.2HCl.PtCl_4$ requires Pt 24·44 per cent.).

—*methoiodide.*—0·15 g. base was treated with 4 mol. methyl iodide in 3 c.c. chloroform solution. The reaction did not proceed at room temperature as quickly as in case of the other bases of the series, but a deposit of colourless crystals settled down overnight, which developed farther on adding a little benzol to the solution. After keeping it again overnight the crystalline deposit was filtered and washed repeatedly with chloroform, m.p. 283-85°. The residue from the filtrate gave through benzol the main quantity of the methoiodide as a white crystalline powder which after being well washed with benzene melted with frothing at 286-87° (total yield, 0·18 g.). On analysis this was found to be the mono methoiodide of the tetra N-methyl holarrhimine, which apparently does not easily add a sixth methyl owing to the existing load of the N-methyl groups in the molecule. (Found: $N-CH_3$, 14·15; I, 24·37; $C_{26}H_{47}ON_2I$ requires for 5 methyls CH_3, 14·15; I, 23·95 per cent.). The mono methoiodide is easily soluble in alcohol, sparingly in water, and on evaporating down the aqueous solution forms a network of slender needles. On slow evaporation it crystallises out in aggregates of stout prismatic rods and conical prisms.

Benzoyl tetra N-methyl holarrhimine.—0·15 g. base was shaken up with 20 per cent. caustic soda solution and 5 c.c. (10 mols.) of benzoyl chloride at room temperature. To the reaction mixture was added a large quantity of water and the insoluble, white cheesy mass was taken up in ether and shaken out with dil. HCl and water. On making the acidic solution alkaline with caustic soda, without first removing the dissolved ether, the benzoyl base came out as a white crystalline mass, which when washed with water and dried, melted at 170-72°. On recrystallisation from a mixture of ether and petroleum ether it came out in brooms and stars of broad tapering needles, soluble in alcohol and ether, less so in petroleum ether and melting sharply at 176° (Yield, 0·15g.) (Found: C, 77·54; H, 9·8; N, 5·93; $C_{25}H_{43}N_2OC.C_6H_5$ requires C, 78·04; H, 9·75; N, 5·69 per cent.).

—*hydrochloride* came out on bringing together the components in ethereal solution as an oil. On washing with acetone and drying *in vacuo* it formed a hygroscopic white crystalline powder, shrinking at 163° and melting with frothing at 237-38°. It is exceedingly soluble in alcohol and water, but on adding dil. HCl to the aqueous solution it is thrown out as a snow-white mass formed of aggregates of slender tapering needles. (Found: Cl, 12.33; $C_{25}H_{43}N_2CO.C_6H_5HCl$ requires Cl, 12.56 per cent.).

—*picrate* prepared by adding aqueous picric acid to the aqueous solution of the hydrochloride formed a lemon-yellow crystalline powder, fairly soluble

in acetone and alcohol, very sparingly in water. It gave off moisture from 105-160° and frothed up with darkening at 205-210°.

Acetylation of tetra N-methyl holarrhimine.—A mixture of 0·1 g. substance, 0·2 g. sodium acetate (freshly dehydrated) and 0·5 c.c. acetic anhydride was heated in a water-bath for 3 hours. On working up the straw-coloured reaction mixture and liberating the base with caustic soda, it came out as a sticky semisolid which was taken up in ether and dried over sodium sulphate. On removal of the solvent a crystalline residue was left, which when washed with the least amount of cold acetone and dried formed a white crystalline powder softening at 134°, melting sharply at 139-40° to a straw-coloured liquid (yield, 0·08 g.). In contrast to the un-acetylated base it is readily soluble in ether and petroleum ether, slightly less so in acetone and crystallises on evaporation of the solvents in aggregates of stout rods. (Found: C, 76·02; H, 10·04; $C_{25}H_{43}ON_2$ $CO.CH_3$ requires C, 75·32; H, 10·69; $C_{25}H_{44}ON_2$ requires C, 77·3; H, 11·3 per cent.)

—*hydrochloride* came out on adding ethereal hydrochloric acid to the ethereal solution of the base as an oil, which when washed repeatedly with ether and evacuated formed a white hygroscopic powder. It appeared to give off water with frothing from 230° onwards forming a porous skeleton which abruptly melted with darkening and frothing at 273°.

—*picrate* was obtained on adding aqueous picric acid to an aqueous solution of the hydrochloride. It forms a brilliant yellow crystalline powder fairly soluble in alcohol and acetone, sparingly in water. After drying in air it appeared to give off water 105° onwards, gradually stuck to the sides, and melted down at 160° to an orange-coloured treacle which frothed up with blackening at 202-5°.

Tetra N-methyl holarrhimine.

THE ALKALOIDS OF HOLARRHENA ANTI-DYSENTERICA.

Part V. Studies in Holarrhimine.

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The relation between conarrhimine, $C_{21}H_{31}\cdot{}^{NH}_{NH}$ and holarrhimine, $C_{21}H_{31}\cdot{}^{NH_2}_{NH_2}{}^{OH}$, suggested in the earlier communication[1] made it desirable to extend the studies in holarrhimine beyond the position arrived at in Part IV, wherein tetra N.methyl holarrhimine and its benzoyl and acetyl derivatives were characterised, and the action of nitrous acid on holarrhimine was qualitatively observed to yield a nitrogen-free, oily product. The present paper gives the results of studies in methylation, benzoylation and acetylation of holarrhimine.

On treatment of holarrhimine with 4 mols of benzoyl chloride, di- and tri- benzoyl derivatives were formed, and with large excess of acetic anhydride and sodium acetate a tri-acetyl derivative was obtained. With 2 mols of methyl iodide, holarrhimine dimethyliodide was obtained which, however, unexpectedly yielded monomethyl holarrhimine on treatment with caustic soda or silver hydroxide, probably as a result of splitting of one molecule of methyl alcohol in the process of liberation of the base.

$$C_{21}H_{31}\cdot{}^{NH_2CH_3I}_{NH_2CH_3I} + 2KOH = C_{21}H_{31}\cdot{}^{NHCH_3}_{NH_2} + 2KI + CH_3OH + H_2O$$

The analysis of the non-nitrogenous product, obtained through the action of nitrous acid on holarrhimine and expected to correspond to the formula $C_{21}H_{34}O_3$ gave too high carbon value for this formula. This may probably be due to its slight impurity with a product resulting from a subsequent splitting of a molecule of water. As the substance could not so far be obtained in a pure condition, its description is not included in the practical. It may,

[1] *Proc. Ind. Acad. Sci.*, 1935, **2**, 426.

however, be stated here that this product as well as holarrhimine showed, like conessine, the presence of only one double bond, on titration with bromine. But in each case the brominated products gave on isolation and analysis too low bromine value due probably to a subsequent partial splitting of one HBr, as has been noted in the case of conessine.[2]

It was intended to study holarrhimine more closely but as one of us (R.S.) had to leave for foreign studies, these joint investigations had to be brought to an abrupt close.

2. *Experimental.*

Benzoylation of holarrhimine: Tri-benzoyl holarrhimine.—To a solution of holarrhimine (0·5 g. 1 mol) in 3 c.c. pyridine was added benzoyl chloride (0·85 g. 4 mols) with ice cooling and stirring and the reaction mixture was left well corked at room temperature for two hours. On dilution with water a non-basic crystalline mass separated out which was well washed with water and acetic acid to remove any unchanged base. On recrystallisation from chloroform it formed snow-white hexagonal rods m.p. 269-70° (yield, 0·85 g.). It is soluble in ethyl acetate, alcohol, chloroform and insoluble in ether and petroleum ether (Found: C, 78.45, 78·20; H, 7·60, 7·64; N, 4·57; $C_{21}H_{33}ON_2$. $(CO.C_6H_5)_3$ requires C, 78·26; H, 7·45; N, 4·35 per cent.).

Di-benzoyl holarrhimine.—The mother liquor from tri-benzoyl holarrhimine gave on removal of the solvent the dibenzoyl product as a semi crystalline white powder (0·10 g.) which was easily soluble in ether, petroleum ether and other organic solvents and frothed up at 115°. (Found: C, 77·74; H, 7·77; N, 4·64; $C_{21}H_{34}ON_2$. $(CO.C_6H_5)_2$ requires C, 77·77; H, 8·14; N, 5·14 per cent.).

Acetylation of holarrhimine: Tri-acetyl holarrhimine.—An intimate mixture of holarrhimine (0.5 g.), anhydrous sodium acetate (2 g.) and acetic anhydride (2 c.c.) was heated on the water-bath for two hours. On dilution and further heating on the water-bath a non-basic mass was obtained, which crystallised out of alcohol and ethyl acetate in clusters of spindle-shaped needles melting at 240-41°. On recrystallisation from methyl alcohol and acetone it formed snow-white spindle-shaped needles melting at 249-50° (yield, 0·75 g.). It is soluble in benzene, chloroform, acetone, alcohol, and insoluble in ethyl acetate, ether and petroleum ether. On dehydration at 100° *in vacuo* over P_2O_5 it lost 3·7 per cent. water of crystallisation. $C_{21}H_{33}ON_2.(CO.C_6H_5)_3+H_2O$ requires H_2O, 3·1 per cent. (Found: C, 69·87, 69·90; H, 9·34, 9·20; N, 6·00; $C_{21}H_{33}ON_2.(CO.C_6H_5)_3$ requires C, 70·74; H, 9·17; N, 6·30 per cent.).

[2] *Arch. Pharm.*, 1918, **256**, 57.

Bromination of holarrhimine : Di-bromo holarrhimine.—0·2 g. holarrhimine dissolved in dry chloroform was titrated against bromine in dry chloroform solution with ice cooling, when it took up 0·10 g. bromine (calculated for one double bond 0·10 g.). The titration was followed by means of potassium iodide starch paper. After titration the bromo compound was completely precipitated by adding ether to the mixture. Well washed with ether it melted at 290-95°. On liberation with caustic soda from its acetic acid solution, the bromo base melted at 226-28° (decomp.). It was soluble in alcohol and water and insoluble in chloroform, acetone, ethyl acetate, ether and petroleum ether (Found : C, 51·99 ; H, 7·98 ; N, 5·43 ; Br, 28·32 ; $C_{21}H_{36}ON_2Br_2$ requires C, 51·20 ; H, 7·33 ; N, 5·69 ; Br, 32·5 per cent.).

Methylation of holarrhimine with methyl iodide : Di-methyl holarrhimine hydroiodide.—To a solution of holarrhimine (1 g.) in dry chloroform was added a chloroformic solution of methyl iodide (1 g. 2·3 mols) and the reaction mixture kept overnight at room temperature when a crystalline product separated out, m.p. 276°. On recrystallisation out of alcohol it melted at 278°. It was soluble in warm alcohol and water, insoluble in acetone, ethyl acetate and chloroform (Found : C, 44·84 ; H, 7·13 ; N, 4·54 ; CH_3, 5·93 ; $C_{21}H_{36}ON_2(CH_3I)_2$ requires C, 44·80 ; H, 6·82 ; N, 4·55 ; CH_3 for 2 N–CH_3, 4·87 per cent.).

Methyl holarrhimine.—The aqueous solution of the hydroiodide gave on liberation with ammonia or caustic soda a very small quantity of a white precipitate which after crystallisation from methyl alcohol and ether formed snow-white needles melting at 170° (Found after dehydration at 100° *in vacuo :* C, 74·92 ; H, 10·82 ; N, 8·33 ; $C_{22}H_{38}ON_2$ requires C, 76·30 ; H, 10·98 ; N, 8·09 ; per cent.). A more quantitative yield was obtained on liberation of the base with freshly precipitated silver hydroxide. The base, thereby obtained, also melted at 169-70° and gave no depression with the base liberated with caustic soda. It showed the presence of only one N—CH_3 after Herzig and Meyer (Found : CH_3, 3·91 ; $C_{22}H_{38}ON_2$ requires for 1 N—CH_3, CH_3, 4·32 per cent.). (Found in air dried substance : C, 71·9 ; H, 10·7 ; N, 7·1 ; $C_{22}H_{38}ON_2+H_2O$ requires C, 72·5 ; H, 11·0 ; N, 7·7 ; after dehydrating at 100° : C, 75·0, 75·1 ; H, 11·0, 11·2 ; N, 7·8, 7·8 ; $C_{22}H_{38}ON_2$ requires C, 76·3 ; H, 11·0 ; N, 8·1 per cent.). The dehydration at 100° was apparently not complete.

—*hydrochloride* was obtained by adding ethereal hydrochloric acid to a solution of the base in methyl alcohol and acetone as a white semi-crystalline powder which melted at 266° (decomp.) and was soluble in alcohol and water (Found : Cl, 16·16 ; $C_{22}H_{38}ON_2.2HCl$ requires Cl, 16·95 per cent.).

—*chloroplatinate* was obtained as a golden yellow powder, when a 10 per cent. solution of platinic chloride was added to an aqueous solution of the hydrochloride. It was soluble in alcohol and water and melted at 245° with blackening and decomposition (Found : Pt, 25.6 ; $(C_{22}H_{38}ON_2.2HCl).PtCl_4$ requires Pt, 25·8 per cent.).

—*picrate* was prepared by adding ethereal picric acid to a solution of the base in methyl alcohol and acetone. It crystallises out of alcohol and water in tufts of lemon-yellow needles, sparingly soluble in hot water, fairly soluble in alcohol and melting at 205°.

DERIVATIVES OF SALICYLIC ACID—PART X.

Stability of the Sulphonic Acid Group in the 4-Sulphosalicylic Acid. Part II.—Bromination of 4-Sulphosalicylic Acid.

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(Communicated by Dr. T. S. Wheeler, Ph.D., F.I.C., F.Inst.P., M.I.Chem.E.)

In continuation of Part I "Nitration of 4-sulpho salicylic acid"* the action of bromine on 4-sulphosalicylic acid has been studied.

The action of halogens on sulphonic acids has been studied by Kelbe[1] who has obtained tetrachloro-cymene from cymene sulphonic acid ; by Meyer[2] who has obtained *p*-dichlorobenzene from *p*-chlorobenzenesulphonic acid ; by Sudborough and Lakhumalani[3] who obtained aminochlorobenzene from aminobenzenesulphonic acid. The same reaction has also been studied with regard to 5-sulphosalicylic acid. It has been found that the sulphonic acid group is readily substituted by halogens ; if the reaction is carried further phenols are obtained by the substitution of the -COOH group by halogens. Rusiklal Datta and Mitter[4] have shown that on chlorination 5-sulphosalicylic acid gives 3 : 5-dichlorosalicylic acid. Datta and Bhoumik[5] obtained 2 : 4 : 6-tribromophenol by the action of bromine on the same sulpho acid. F. Sakellarios[6] has converted potassium-hydrogen-3-nitro-5-sulphosalicylate by the action of bromine into 4 : 6-dibromo-2-nitrophenol.

With a view to study the stability of the sulphonic acid group in 4-sulphosalicylic acid (I), it was treated with bromine when bromosulphosalicylic acid (II), dibromosulphosalicylic acid (III) and tribromosulphosalicylic acid (IV) were obtained. It is interesting to note that even with excess of bromine the reaction does not proceed further and neither the $-SO_3H$ nor -COOH is eliminated.

In view of the combined directing influences of -OH and -COOH groups in salicylic acid and also the preference for the position -5 over that of -3, the constitution of the above described acids follow, as shown in the diagram.

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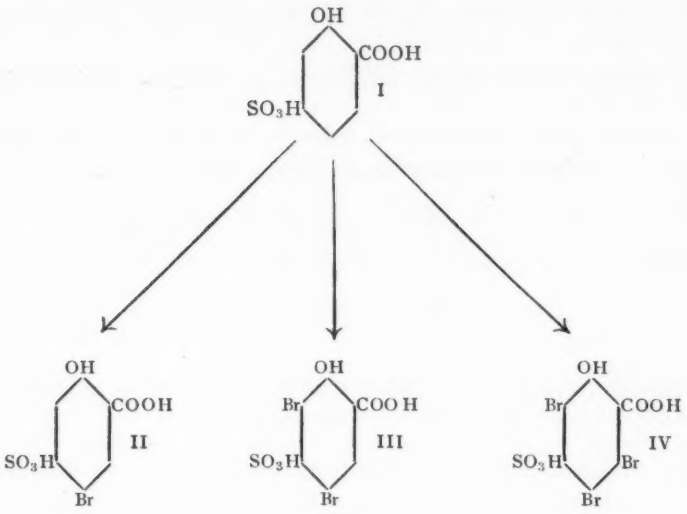
* *Proc. Ind. Acad. Sci.*, 1936, **3**, 236.



The stability of both the $-SO_3H$ and -COOH groups and the absence of a tribromophenol-*m*-sulphonic acid similar to trinitrophenol-*m*-sulphonic acid† finds an easy explanation in the combination of the directing influences of -OH and -COOH on the one hand and $-SO_3H$ and Br on the other in the same molecule.

The first bromine enters position -5 and gives (II) in obedience to the combined influence of -OH and -COOH in spite of the opposing influence of $-SO_3H$. Similarly the second bromine enters the position -3 and gives (III). But when (III) is now further brominated, the combined influences of $-SO_3H$ (*m*), -Br (*o*), and Br (*p*), become stronger than that of the -OH (*o*) and thus the third bromine enters position -6 and does not eliminate the -COOH group. Thus for the sum of the directing influences we have, OH + COOH > Br + SO_3H and Br + SO_3H + Br > OH + the resistance from -COOH.

The stability of the $-SO_3H$ group depends on where it is placed in the molecule. If it is subjected to stronger directing influences as with 3-sulphosalicylic acid or 5-sulphosalicylic acid it is easily substituted either by $-NO_2$ group or by bromine, but if it is outside this influence as with 4-sulphosalicylic acid its substitution by these groups becomes impossible. Similarly the -COOH group which is eliminated in nitration is completely protected in bromination.

† *Proc. Ind. Acad. Sci.*, 1936, **3**, 236.

Experimental.

Bromination of 4-sulphosalicylic acid :—

4-*Sulpho*-5-*bromosalicylic acid*.—Bromine (10 g.) vapour was passed into 4-sulphosalicylic acid (13 g.) dissolved in water (50 c.c.) and the mixture kept overnight. The solid obtained on evaporation was pressed on a porous tile and dried over sodium hydroxide to remove hydrobromic acid. It crystallises from a little water in needles with four molecules of water ; m.p. 210°. It is not hygroscopic. (Found : Equivalent, 181·8 ; S, 8·6 ; Br, 22·1 ; H_2O, 19·4. $C_7H_5O_6SBr$, $4H_2O$ requires equivalent, 184·5 ; S, 8·7 ; Br, 21·6 ; H_2O, 19·5 per cent.)

Neutral barium-4-*sulpho*-5-*bromosalicylate*—which was obtained by neutralising the acid with barium carbonate, crystallised from water as grey white powder, with four molecules of water of which three can be driven out at 200° under reduced pressure. It turns pale yellow on heating. (Found : Ba, 27·3 ; H_2O, 10·8 ; $C_7H_3O_6SBrBa$, $4H_2O$ requires Ba, 27·2 ; H_2O, 14·3 per cent. and $C_7H_3O_6SBrBa$, $3H_2O$ requires Ba, 28·2 ; H_2O, 11·1 per cent.)

Acid potassium-4-*sulpho*-5-*bromo-salicylate*.—The acid was neutralised and strongly acidified with hydrochloric acid. On concentration a salt separated which crystallised from water in white needles. (Found : K, 11·7 ; $C_7H_4O_6SBrK$ requires K, 11·6 per cent.)

4-*Sulpho*-3 : 5-*dibromo-salicylic acid*—was prepared as described for the monobromo acid using twice the quantity of bromine. It was more soluble in water than the mono-bromo-acid and crystallised in long white needles with m.p. 83°. It was hygroscopic and so it was kept over $CaCl_2$ for analysis. (Found : S, 7·0 ; Br, 35·6 ; H_2O, 15·9 ; equivalent, 222·7 ; $C_7H_4O_6SBr_2$, $4H_2O$ requires S, 7·2 ; Br, 35·7 ; H_2O, 16·1 per cent. ; equivalent, 224·0.)

Acid potassium-4-*sulpho*-3 : 5-*dibromo-salicylates*—was obtained by acidifying a solution of the neutral salt. It crystallised from water in white needles. (Found : K, 9·5 ; $C_7H_3O_6SBr_2K$ requires K, 9·4 per cent.)

Neutral barium-4-*sulpho*-3 : 5-*dibromo-salicylate*—was prepared by neutralising the acid with barium carbonate. It crystallised from water as microscopic grey needles, with one molecule of water. (Found : Ba, 26·2 ; H_2O, 3·2 ; $C_7H_2O_6SBr_2Ba$, H_2O requires Ba, 26·0 ; H_2O, 3·4 per cent.)

4-*Sulpho*-3 : 5 : 6-*tribromo-salicylic acid* was prepared as described for the monobromo acid using three times the quantity of bromine. The solid obtained on concentration contained hydrobromic acid which was removed under reduced pressure at 100°. The residue, after pressing on a porous tile and drying over alkali, crystallised from water in needles, m.p 115°,

(Found : S, 7·2 ; Br, 53·0 ; equivalent, 227·5 ; $C_7H_3O_6SBr_3$ requires S, 7·0 ; Br, 52·7 per cent. ; equivalent, 227·4.)

Neutral barium-4-sulpho-3 : 5 : 6-tribromo-salicylate—was obtained by neutralising the acid with barium carbonate. It crystallised from water in microscopic grey needles, with two molecules of water. (Found : Ba, 22·0 ; H_2O, 5·5 ; $C_7HO_6SBr_3Ba$, 2 H_2O requires Ba, 21·9 ; H_2O, 5·7 per cent.)

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Summary.

4-Sulphosalicylic acid gave on bromination (I) 4-sulpho-5-bromosalicylic acid, (II) 4-sulpho-3 : 5-dibromosalicylic acid, (III) 4-sulpho-3 : 5 : 6 : tribromosalicylic acid.

The experimental results indicate that the relation of the directing influences is as follows :—

$$OH + COOH > Br + SO_3H$$

and

$$Br + SO_3H + Br > OH + \text{resistance of -COOH.}$$

REFERENCES.

1. Kelbe, *Ber.*, 1883, **16**, 617.
2. Meyer, *M.*, 1915, **36**, 719.
3. Sudborough and Lakhumalani, *J. C. S.*, 1917, **111**, 41.
4. Rusiklal Datta and Mitter, *J. Amer. Chem. Soc.*, 1919, **41**, 2037.
5. Datta and Bhoumik, *J. Amer. Chem. Soc.*, 1921, **43**, 311.
6. E. Sakellarios, *Ber.*, 1922, **55B**, 2846-2853.

THE TRACKS OF THE α-PARTICLES OF THORIUM AND ITS PRODUCTS.

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It has been known for many years[1] that α-particles can be recorded by allowing them to pass through a photographic emulsion. The emulsion consists of numerous grains of silver bromide, embedded in gelatine, and an α-particle traversing the emulsion will pass through those grains which lie on its path. These grains are affected by the α-particle, in much the same way as they are affected by light in the ordinary photographic process. When the plate is developed, these grains are accordingly reduced by the chemical action of the developer, and become grains of solid silver. Unaffected grains are dissolved out by a solution of hypo. In the developed plate, therefore, the paths of α-particles which have passed through the emulsion are visible as rows of black grains. A high magnification is necessary for observing these tracks.

More recently the technique has been improved, and the method has been applied in several investigations.[2,3,4,5,6] Special plates are used, coated with the new Ilford " R " emulsion. This emulsion is specially suitable for recording α-particle tracks, and was originally prepared in the Ilford laboratories for this purpose.[7] The grains are very small, the mean diameter being only $0{\cdot}3\,\mu$. The stopping power of the emulsion for α-particles is about 1400 times greater than that of air ; one cm. path in air is equivalent to $7\,\mu$ in the emulsion, and the mean number of grains in a path of this length is five. The number of grains corresponding to a given length of path is naturally subject to considerable variations.

In order to record the tracks of the α-particles emitted by thorium and its products, the following method was used. A weak solution of thorium nitrate was prepared, and a plate was placed in the solution for about twenty minutes. The plate was then removed and dried, all the operations, of course, being carried out in complete darkness in order to avoid fogging.

When the plate dries, the solute remains in the gelatine, so that thorium atoms are distributed uniformly through the emulsion. These atoms remain in practically fixed positions during the progress of the experiment. After an interval of three days, the plate was developed and fixed in the normal manner, and after drying was examined microscopically. (For this purpose we use a fluorite dry objective corrected for use with uncovered objects, N.A. $= 0{\cdot}90$, and a total magnification of 900 ×. It is impracticable to use an oil-immersion objective.)

Many more tracks are observed than can be ascribed to thorium alone, since all the members of the thorium series are present. In the complete transformation from thorium to thorium D, an atom emits six α-particles. The series is well known, and the relevant data are given in the following table :

Element	Type of Disintegration	Range of α-particle in cms. air at 18°C.	Decay constant	Half-value period
Thorium	α	2·93	$1{\cdot}33\times10^{-12}$ sec.$^{-1}$	$1{\cdot}65\times10^{10}$ years
Mesothorium I	β		$3{\cdot}28\times10^{-9}$	6·7 years
Mesothorium II	β		$3{\cdot}14\times10^{-5}$	6·1 hours
Radiothorium	α	4·05	$1{\cdot}16\times10^{-8}$	1·9 years
Thorium X	α	4·40	$2{\cdot}20\times10^{-6}$	3·6 days
Thorium Emanation	α	5·11	$1{\cdot}27\times10^{-2}$	54·5 secs.
Thorium A	α	5·74	4·78	0·14 secs.
Thorium B	β		$1{\cdot}82\times10^{-5}$	10·6 hours
Thorium C	α & β	4·82	$1{\cdot}91\times10^{-4}$	60·5 mins.
Thorium C′	α	8·70	ca. 10^{11}	very short
Thorium C″	β		$3{\cdot}61\times10^{-3}$	3·2 mins.
Thorium D	stable			

The series branches at Th. C, which disintegrates *either* with the emission of an α-particle, to give Th. C″, *or* with the emission of a β-particle, to give Th. C′. Thus the α-particles of Th. C and Th. C′ are alternative ; in the

course of its disintegration an atom emits either one or the other, but not both.

Let us suppose that a particular atom of thorium in the emulsion emits its α-particle. The chance that the same atom will emit a further α-particle during the period of the experiment is very small. Indeed it will be several years before any appreciable fraction of the atoms have reached the stage of emitting the next α-particle, since the half-value periods of MsTh. I and RdTh. are large. The tracks should therefore occur singly, and several tracks radiating from a single point are not to be expected. Many such single tracks due to the α-particles of thorium are actually observed.

Radiothorium is an isotope of thorium, and is probably present in the original solution in the equilibrium amount. This element is thus introduced into the emulsion with the thorium, and the amount of RdTh. present will not vary appreciably during the period of the experiment. We can therefore calculate the amounts of the subsequent products which are present at any later time. Let the decay constants of a series of consecutive elements be denoted by $\lambda_1, \lambda_2, \lambda_3 \ldots\ldots$ and suppose that the first element is the only one which is present initially. Then the amount of the nth element at the time t is given by the expression

$$N(t) = c_1 e^{-\lambda_1 t} + c_2 e^{-\lambda_2 t} + \ldots\ldots\ldots\ldots\ldots + c_n e^{-\lambda_n t}$$

where
$$c_1 = N_0 . \lambda_1 \lambda_2 \ldots\ldots \lambda_{n-1} / (\lambda_2 - \lambda_1)(\lambda_3 - \lambda_1)\ldots\ldots(\lambda_n - \lambda_1)$$
$$c_2 = N_0 . \lambda_1 \lambda_2 \ldots\ldots \lambda_{n-1} / (\lambda_1 - \lambda_2)(\lambda_3 - \lambda_2)\ldots\ldots(\lambda_n - \lambda_2)$$
$$\ldots\ldots\ldots\ldots\ldots \text{etc.}$$

N_0 = number of atoms present initially.

We are chiefly interested in the amounts of the elements Th. X, Th. B, and Th. D which are present in the emulsion, since the short-lived elements will be present only in infinitesimal amounts. Before an atom of Th. X can be formed, its parent RdTh. atom must have emitted an α-particle, so that every Th. X atom present should be the point of origin of a single track in the emulsion. Before an atom of Th. B can be formed, four α-particles must be emitted, and therefore every Th. B atom present should be at the point of origin of four tracks. Similarly, five tracks should radiate from every Th. D atom present.

If the calculation be made, for example, with $t = 3 \cdot 10^5$ seconds ($= 3\frac{1}{2}$ days, the approximate exposure in the experiments), we find the relative numbers of atoms are as follows:

Th. X (origin of a single track)	25
Th. B (centre of a "star" of four tracks)	2·6
Th. D (centre of a "star" of five tracks)	31

In the original solution, some of the later products of disintegration (Th. X and Th. B) are already present, though not necessarily in equilibrium amount. These will give some additional tracks. The transition Th. X→Th. B will produce a "star" of three tracks; the transition Th. X → Th. D will produce a "star" of four tracks; and the transition Th. B → Th. D will give a single track, either long (8·7 cms.) or short (4·8 cms.)

It is clear, then, that a plate should show, on examination:

(*a*) Single tracks corresponding to the α-particles of Th.

(*b*) A number of "stars" consisting of five tracks radiating from a point.

(*c*) A somewhat smaller number of single tracks corresponding to the α-particles of RdTh.

(*d*) A few "stars" of three or four tracks.

(*e*) A few single tracks corresponding to the α-particles of Th. C and Th. C′.

The observations confirm these conclusions. It is not possible, however, to check the relative numbers of single tracks and "stars", except very roughly. The reason for this is that the atoms are situated at all depths in the emulsion, and the α-particles are emitted in all directions. Only tracks lying in or near the horizontal plane are suitable for measurement, and as many of the α-particles pass out of the emulsion altogether, their tracks are incomplete. This will be easily understood when it is remembered that the thickness of the emulsion does not exceed 14 μ, the equivalent of 2 cms. of air.

The identification of individual tracks presents great difficulty. It has been pointed out previously that the tracks corresponding to α-particles of a given energy show considerable variations in length, and a critical discussion of these variations has been given.[6] If a large number of tracks, produced by α-particles of the same energy, are measured, a frequency curve of the measurements can be constructed. From this curve it is possible to obtain a quantity known as the "extrapolated length" of the tracks, which can be determined with some accuracy, and which is strictly proportional to the range in air of the same particles. From the measurement of a *single* track, however, there is a large uncertainty in the determination of the corresponding range in air. In a "star" of five tracks, usually only the long track corresponding to the Th.C′ α-particle (8·7 cms.) can be identified with certainty. The ranges of the other α-particles do not differ sufficiently for the tracks to be distinguished unambiguously.

Many hundreds of " stars " have been observed. In order to obtain a photomicrograph of a " star ", all five tracks must be approximately in the horizontal plane, and the central point must not be too near the surface of the emulsion, or some tracks may fail to be recorded. The probability that an individual track will lie sufficiently near the horizontal plane for this purpose is certainly not more than $\frac{1}{3}$, and the probability that all the five tracks will be complete and well-placed for photomicrography is probably not more than 1/50,000. One can therefore hardly expect to find a perfect specimen. After some weeks of careful searching two " stars " have been found, however, in which the conditions are nearly fulfilled. These are shown in the diagram (Figs. 1 and 2), which may be compared with the photomicrographs (Figs. 3 and 4). Measurements of the tracks give the following results :

Track	Length in μ	Calculated range in cms. of air	Remarks
Figs. 1 & 3—			
a	57	8·51	α-particle of Th. C′
b	28·5	4·26	
c	26·3	3·93	
d	..	..	track incomplete
e	28·5	4·26	
Figs. 2 & 4—			
a	56	8·36	α-particle of Th. C′
b	34	5·08	? Th. Em. or Th. A
c	29	4·33	
d	6·3	..	track incomplete
e	..	..	track out of focus

The chief interest of the present observations lies in the fact that we have the whole history of an isolated radioactive atom, recorded as a "star" in the emulsion. Other methods of studying radioactive transformations, on the other hand, give only the "average history" of a large number of atoms, or else, as in the Wilson chamber, give a record of the transformations occurring during a very small interval of time.

There is some evidence that an atom may occasionally diffuse through the emulsion for a perceptible distance during the progress of the experiment. Occasionally instances are found in which the five tracks belonging, apparently, to the same "star", do not diverge from exactly the same origin. This suggests that the atom has moved, say, in the time between the emission of the first α-particle and the emission of the last four. The extent of this apparent movement is not more than three or four μ. This is a point, however, upon which it is difficult to come to any certain conclusion, for the

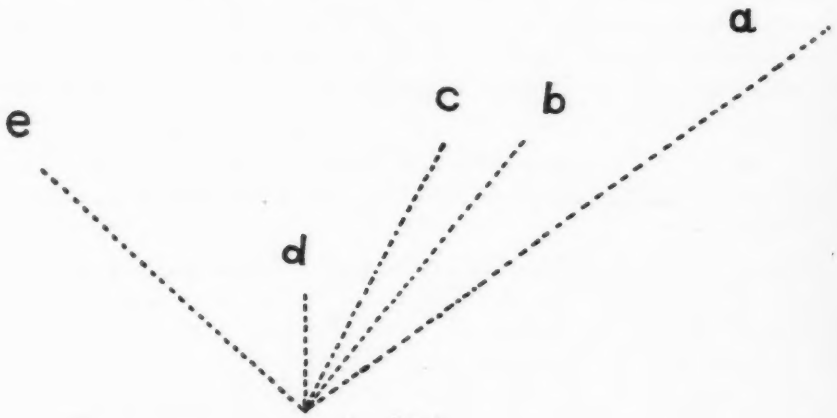

FIG. 1.

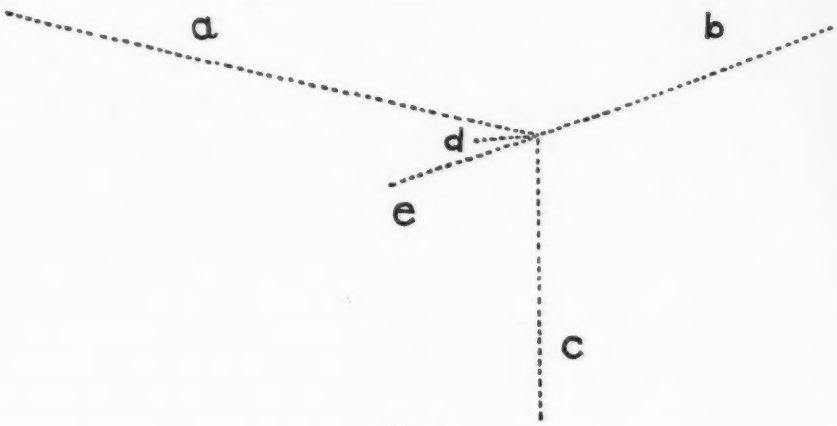

FIG. 2.

FIG. 3. Magnification ×1135

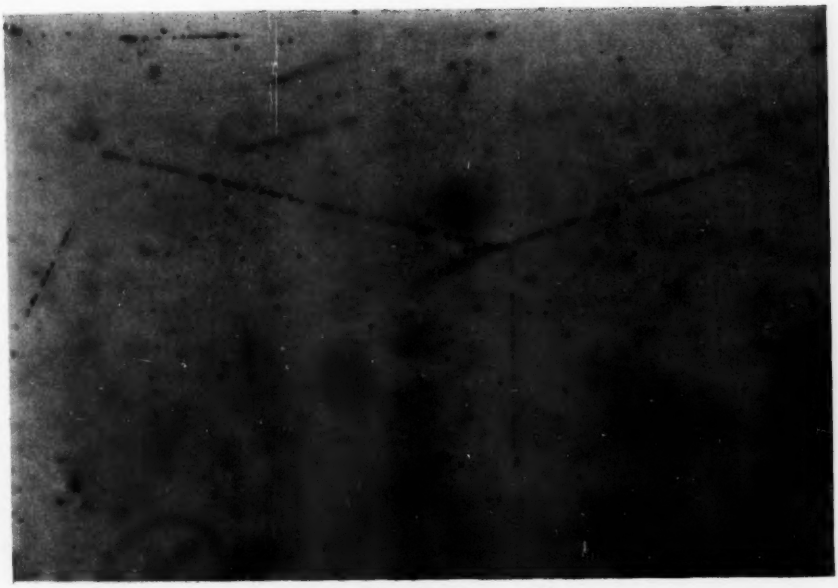

FIG. 4. Magnification ×1135

tracks are not continuous lines, and the path of an α-particle does not necessarily pass through the centre of a grain. If an α-particle merely grazes the edge of a grain, this grain appears, to the eye, somewhat displaced. It is therefore very difficult to be quite sure that the tracks do not, in reality, diverge from the same point. Furthermore the effect might be simulated by the slight scattering of an α-particle after it had travelled a short distance through the emulsion; and there is always the possibility that the displaced track is really an independent single track, not connected with the "star". Taking these possibilities into account, one is nevertheless led to the view that an appreciable displacement of the atoms does actually occur, though it is not sufficiently definite to lead to any quantitative information on the diffusion of heavy atoms in gelatine.

A noteworthy point is that "stars" of more than five tracks are very infrequent, indicating that the molecules of radiothorium nitrate are deposited singly in the emulsion, and do not tend to associate in groups. Very infrequently a " star " of perhaps a hundred tracks may be found, which must be due to a group of many molecules. Possibly under certain circumstances there is a kind of incipient crystallisation in the gelatine. This, however, is quite exceptional, and as a rule is not found.

In conclusion, we wish to express our thanks to Lord Rutherford for his continued interest in these experiments.

Summary.

The tracks of the α-particles from members of the thorium series have been recorded in a photographic emulsion, by the use of a technique previously developed. Radiothorium atoms introduced into the emulsion disintegrate *in situ*, emitting five α-particles in succession. In this way " stars " are produced, consisting of five tracks radiating from a point, of which a discussion is given. Photomicrographs of two " stars " are reproduced.

REFERENCES.

1. Kinoshita, *Proc. Roy. Soc.*, A, 1910, **83**, 432; and subsequent papers.
2. Taylor and Goldhaber, *Nature*, March 2, 1935, **135**, 341.
3. Taylor, *Proc. Roy. Soc.* A, 1935, **150**, 382.
4. Taylor, *Proc. Phys. Soc.*, 1935, **47**, 873.
5. Taylor, *Nature*, Nov. 2, 1935, **136**, 719.
6. Taylor and Dabholkar, *Proc. Phys. Soc.*, 1936, **48**, 285.
7. Ilford, Ltd., *J. Scientific Instr.*, 1935, **12**, 333.

ON THE THEORY OF PRESSURE BROADENING OF SPECTRAL LINES.

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Introduction.

The asymmetric broadening and shift of spectral lines under foreign gas pressure are ascribed to perturbations of the energy levels of the excited atoms, due partially to their coupling with the same set of virtual oscillators of the foreign gas, which determine its dispersion. These "dispersion forces" have been first considered in this connection by Margenau.[1] A shorter and more general treatment of these forces is possible, which yields a simple relation between the refractive index of the perturbing gas and the red shift produced by these interactions. (Section I.)

Width and violet shift may be partially due to coupling interactions of a more general type, which would depend to some extent upon the alteration of the relative positions of perturbing and radiating atoms. (Section II.)

The equations describing varying interactions can be solved by successive approximations. This method allows a simultaneous treatment of impact broadening and statistical distribution of the frequency displacements, which have been usually treated as formally distinct (v. e. g.[2]). (Section III.)

I.

We base our considerations on the set of equations

$$(1)\quad \ddot{q}_i + 2x_i\dot{q}_i + \omega_i^2 q_i + \sum_j (j \neq i)\,(a_{ij}\ddot{q}_j + 2k_{ij}\dot{q}_j + b_{ij}q_j) = F(t)$$

where x_i is the transition probability for the i-th oscillator in case of vanishing interaction, ω_i its characteristic frequency and $F(t)$ an external force. Holtsmark's,[3] Mensing's [4,5] and Frenkel's [6] theory of resonance broadening is based upon equations of the same form containing only the coupling coefficients b_{ij}. A possible physical interpretation of the coupling forces $a\ddot{q}$ and $k\dot{q}$, which are introduced at present hypothetically, will be discussed in Section II. All the coefficients $a_{ij} = a_{ji}$, etc., since equations (1) can be derived from an energy function.

The electric field strength due to the dipole eq_j at the place of the i-th dipole is

$$|\vec{E}| = \frac{eq_j}{r_{ij}^3} \cdot \sqrt{(1 - 3\cos^2\theta_{ij})^2 + 9\cos^2\theta_{ij}\cdot\sin^2\theta_{ij}}$$

$$= \frac{eq_j}{r_{ij}^3}\sqrt{1 + 3\cos^2\theta_{ij}}$$

where θ_{ij} is the angle between the axis of the j-th dipole and the line joining it with the i-th dipole, r_{ij}. Terms of higher order in $1/r$ are omitted under the assumption that

(2) $r_{ij} \gg q_j$

This electric field strength is represented in (1) by the term $b_{ij}q_j$, which becomes identical with $|\vec{E}|$, when it is multiplied by m/e, m and e being the mass and charge of the electron. We have thus

(3) $b_{ij} = \frac{e^2}{r_{ij}^3 m} \times \sqrt{3\cos^2\theta_{ij} + 1}$

We consider now the interaction of one excited atom, denoted by the index 1, with perturbing, unexcited molecules of the foreign gas. If $\omega_1 \neq \omega_j$ and

(4) $|a_{ij}| \ll 1, |k_{ij}| \ll \omega_1, |b_{ij}| \ll \omega_1^2$

and if, further, all the coupling coefficients can be considered as constant, we easily obtain (v. Courant-Hilbert, *Meth. der math. Phys.*, 1924, p. 231) the additional transition probability

(5) $x' = \sum_{j=2}^{n} \frac{2k_{ij}\,\omega_1^2(a_{1j} - b_{1j}/\omega_1^2)}{\omega_j^2 - \omega_1^2}$

and the frequency displacement

(6) $\Delta\omega = -\frac{1}{2}\omega_1 \sum_{j=2}^{n} \frac{(a_{1j} - b_{1j}/\omega_1^2)^2\,\omega_1^2 - k_{1j}^2}{\omega_j^2 - \omega_1^2}$

terms of higher order in the coupling coefficients being omitted. Since $\omega_j > \omega_1$, if ω_j are the characteristic frequencies of the virtual dispersion oscillators of the foreign gas, we have red shift for

(7) $|a_{1j} - b_{1j}/\omega_1^2|\,\omega_1 > |k_{1j}|$

and violet shift for

(7′) $|a_{1j} - b_{1j}/\omega_1^2|\,\omega_1 < |k_{ij}|$

The red shift due to the electrostatic coupling (3) is

(8) $\Delta\omega = -\frac{1}{2}\cdot\frac{e^4}{m^2}\cdot\frac{1}{\omega_1}\sum_{j=2}^{n}\cdot\frac{1}{r_{ij}^6}\cdot\frac{1}{\omega_j^2 - \omega_1^2}(3\cos^2\theta_{1j} + 1)$

If all the perturbing molecules are identical ($\omega_j = \omega_2$ for $j \neq 1$) and equally distributed, we obtain the average red shift by replacing for the sum the corresponding integral from R_0, the distance of mean closest approach between the excited atom and its perturbers, to infinity:

$$\Delta\omega = -\tfrac{1}{2}\frac{e^4}{\omega_1 m^2}\frac{N}{\omega_2^2-\omega_1^2}\int_{R_0}^{\infty}\int_0^{\pi}\int_0^{2\pi}\frac{1}{r^4}dr\cdot(3\cos^2\theta+1)\sin\theta\cdot d\theta\cdot d\phi$$

where N is the number of foreign gas molecules per unit volume. Evaluating this integral we obtain:

$$(9)\quad \Delta\omega = -\frac{4\pi}{3}\cdot\frac{e^4}{\omega_1 m^2}\cdot\frac{N}{\omega_2^2-\omega_1^2}\cdot\frac{1}{R_0^3}$$

Under the same assumptions, the classical theory of dispersion yields for the refractive index the expression:

$$\mu - 1 = 2\pi\cdot\frac{e^2}{m}\cdot\frac{N}{\omega_2^2-\omega_1^2}$$

Combining it with (9), we obtain

$$(10)\quad \Delta\omega = -\frac{2}{3}\cdot\frac{e^2}{\omega_1 m}\cdot\frac{1}{R_0^3}(\mu-1)$$

If more than one type of virtual oscillators are considered, $N/(\omega_2^2-\omega_1^2)$ has to be replaced by the appropriate sum. (10) is also valid in this case.

The wave-length shift, corresponding to (10), is

$$(11)\quad \Delta\lambda = \frac{4\pi e^2}{3mc^2}\left(\frac{\lambda}{2\pi R_0}\right)^3(\mu-1)$$

According to the classical theory of radiation $\frac{4\pi e^2}{3mc^2}$ is the natural width of spectral lines, say $\Delta_0\lambda$. We have thus

$$(11')\quad \Delta\lambda = \Delta_0\lambda\left(\frac{\lambda}{2\pi R_0}\right)^3(\mu-1)$$

The same result can be obtained in quantum mechanics. For the sake of simplicity we consider again virtual oscillators of only one type. Their variable electric moment, induced by the electric field of the excited atom is (v.e.g. Born-Jordan, *Elementare Quantenmechanik*, p. 246, 17–19.)

$$P^{(j)} = \frac{\mu-1}{2\pi N}\,|\vec{E}|$$

or, since

$$|\vec{E}| = \frac{P^{(1)}}{r_{1j}^3}\sqrt{3\cos^2\theta_{1j}+1},$$

$$P^{(j)} = \frac{\mu-1}{2\pi N}\cdot\frac{P^{(1)}}{r_{1j}^3}\sqrt{3\cos^2\theta_{1j}+1}$$

Putting this expression into

$$E_{1j} = \frac{1}{r_{1j}^3} P^{(1)} \; P^{(j)} \sqrt{3 \cos^2 \theta_{1j} + 1}$$

E_{1j} being the energy of interaction of the two oscillators considered, we obtain

$$E_{1j} = \frac{\mu - 1}{2\pi N} \cdot \frac{P^{(1)2}}{r_{1j}^6} (3 \cos^2 \theta_{1j} + 1)$$

and, dividing by $\hbar$ ($2\pi\hbar$ Planck's constant), the corresponding frequency displacement

$$\Delta\omega = \frac{P^{(1)2}}{\hbar} \cdot \frac{\mu - 1}{2\pi N} \cdot \frac{1}{r_{1j}^6} (3 \cos^2 \theta_{1j} + 1)$$

Integration of this expression yields (10), if we assume

$$P^{(1)} = e \sqrt{\frac{\hbar}{2\omega m}}$$

We notice that this is the absolute value of the element $P_{01}^{(1)}$ of the matrix that describes the electric moment of the linear oscillator. [v. l. c., p. 127, (27)*c*.]

A straightforward test of (10) or (11) is not possible at present, since R_0 has not been evaluated theoretically. Holtsmark[3] assumes in the analogous case in his theory of resonance broadening that R_0 is the gas-kinetic collision radius, but then too great values for the line width are obtained.[7] This assumption is also hardly compatible with condition (2). We shall, therefore, rather investigate whether reasonable values for R_0 are obtained from the observed shift. We calculate R_0 from (11)

$$(12) \quad R_0 = \lambda \sqrt[3]{\frac{1}{6\pi^2} \cdot \frac{e^2}{mc^2} \cdot (\mu - 1) \frac{1}{\Delta\lambda}}$$

or, introducing the numerical values for e, m, c

$$(12') \quad R_0 = \lambda \times 1 \cdot 679 \cdot 10^{-5} \sqrt[3]{\frac{\mu - 1}{\Delta\lambda}}$$

Margenau obtained his mean distance of approach, R_1, from a formula [v. l. c.,[1] (25)] similar to our formula (11). His numerical values for R_1, calculated from the pressure shift of the absorption line Hg 2537, are given in the following table, together with R_0, obtained from (12′)

Perturbing gas	$\Delta\lambda$ for 1 atm.	R_0	R_1	$(\mu - 1) \cdot 10^4$
A	·0088	6·43A	4·8A	3·022
O_2	·0079	6·67	5·0	3·031
CO_2	·0078	7·85	6·2	4·895
H_2	·0042	6·52	4·9	1·547

Since $R_0 \sim 1 \cdot 3\, R_1$, the frequency displacement (10) is, for the same values of the mean distance of approach, more than twice as great as that obtained from Margenau's formula. This result indicates that the influence of the dispersion forces upon the shift of spectral lines may be of greater importance than has been assumed hitherto.

Comparing (10), further, with the shift due to dielectric polarisation of the foreign gas,[8]

$$(13)\quad \Delta\omega \cong -\,9\,\frac{\epsilon - 1}{4\pi} \cdot \frac{e^2}{h}\, N^{\frac{1}{3}}$$

where ϵ is the dielectric constant and $\epsilon - 1 \sim 2\,(\mu - 1)$, we find that the displacements (10) and (13) are, for pressures up to a few atmospheres, of the same order of magnitude, when $R_0 \sim 6\text{-}9 \cdot 10^{-8}$ cm. Since these values are rather large for the mean distance of approach, it is probable that except for very high pressures or great radii of the excited atoms, as for instance in the case of the higher series members of the alkali spectra,[8,9] the red shift is mainly due to dispersion forces.

For the numerical values of R_0 calculated above, condition (4), *viz.*, $b_{1j} \ll \omega_1^2$, is fulfilled, but there may be some doubts concerning the validity of condition (2). If the omission of higher order terms in $1/r$ in (3) were not justified, the displacement calculated from (10) might be too small. The values found for R_0 are, on the contrary, comparatively large. This indicates that it will be perhaps necessary to explain why the observed red shift is not greater, all the more since the displacement due to other perturbations, which also produce usually red shift, is certainly not negligible and has to be added to the coupling displacement. Perhaps this difficulty will disappear if the consideration of the coupling forces $a\ddot{q}$ and $k\dot{q}$ can be justified.

II.

Coupling forces of the type $k\dot{q}$ would be of essential importance for the intensity distribution. It seems to be necessary to consider them, for if $k_{1j} = 0$, the additional transition probability (5) vanishes, and then no transfer of energy to the foreign gas molecules and no forced vibrations of these are possible.

From equations (1) the intensity distribution in absorption lines, which have been chiefly considered hitherto, is easily obtained, provided that the conditions (4) are valid and that all the coupling coefficients are constant. For simplicity we consider only one excited and one perturbing atom. The equations (1) run in this case

$$(14)\quad \begin{aligned} &\ddot{q}_1 + 2x_1\dot{q}_1 + \omega_1^2 q_1 + a\ddot{q}_2 + 2k\dot{q}_2 + bq_2 = F(t) \\ &a\ddot{q}_1 + 2k\dot{q}_1 + bq_1 + \ddot{q}_2 + 2x_1\dot{q}_2 + \omega_2^2 q_2 = F(t) \end{aligned}$$

If the external force $F(t)$ can be represented by a Fourier integral

$$(15)\quad F(t) = \int_{-\infty}^{+\infty} F(\omega)\, e^{i\omega t}\, d\omega$$

an approximate solution is readily obtained. Assuming

$$q(t) = \int_{-\infty}^{+\infty} q(\omega) e^{i\omega t} d\omega$$

and comparing both sides of (13), we get

$$(-\omega^2 + 2x_1 i\omega + \omega_1^2)\, q_1(\omega) + (-\omega^2 a + 2ki\omega + b)\, q_2(\omega) = F(\omega)$$

$$(-a\omega^2 + 2ki\omega + b)\, q_1(\omega) + (-\omega^2 + 2x_2 i\omega + \omega_2^2)\, q_2(\omega) = F(\omega)$$

and hence

$$(16)\quad q_1(\omega) = \frac{F(\omega)\,[1 - H(g + 2ik\omega)]}{-\omega^2 + \omega_1^2 - H(g^2 - k^2\omega^2) + 2i\omega(x_1 - 2Hkg)}$$

$$q_2(\omega) = \frac{F(\omega)\, H[-\omega^2 + \omega_1^2 + 2ix_1\omega - (g + 2ik\omega)]}{-\omega^2 + \omega_1^2 - H(g^2 - k^2\omega^2) + 2i\omega(x_1 - 2Hkg)}$$

where

$$(17)\quad \omega_2^2 + 2x_2 i\omega - \omega^2 = 1/H,\quad -a\omega^2 + b = g$$

An approximate expression for the intensity distribution is obtained by calculating the average value of $F(\omega)\, e^{i\omega t}\, \frac{d}{dt}\,[q(\omega)\, e^{i\omega t}]$, to which only the imaginary part of $q(\omega)$ yields a non-vanishing contribution. Since perceptible absorption occurs only in a narrow frequency interval, we may put $F(\omega_1) = F(\omega)$ and $\frac{\omega}{\omega_1} = 1$. If we suppose, further, $F(\omega_2) = 0$, we may omit x_2. Putting

$$(18)\quad \omega_1' = \omega_1 - \frac{1}{2\omega_1} H(g^2 - k^2\omega^2)$$

and

$$(18')\quad x' = x_1 - 2Hkg$$

we obtain

$$(19)\quad J(\omega) = \text{Const.}\, \frac{x'\,[1 + H(\omega_1^2 - \omega^2 - 2g)] + (\omega_1' - \omega)\, 2H(2k - x_1)}{(\omega_1' - \omega)^2 + x'^2}$$

Terms of order higher than the second in the coupling coefficients can be omitted, if conditions (4) hold. For the same reason ω can be replaced in H, ω_1', and x' by ω_1, since, over the frequency interval considered, $|\omega - \omega_1|$ or $|\omega - \omega_1'| \sim H/2\omega\,|g^2 - k^2\omega^2|$ or $|x_1 - 2Hkg|$. (19) is then reduced to

$$(20)\quad J(\omega) = \text{Const.}\, \frac{x'}{(\omega_1' - \omega)^2 + x'^2}$$

If equations (1) are solved for any number of perturbers, the same formula (20) is obtained with

$$(21)\quad \omega_1' = \omega_1 - \frac{H}{2\omega_1}\sum_{i=2}^{n}\left[(a_{1i}\omega_1^2 - b_{1i})^2 - k_{1i}^2\omega_1^2\right]$$

$$x' = x_1 - 2H\sum_{i=2}^{n} k_{1i}\,(a_{1i}\omega_1^2 - b_{1i})$$

in full agreement with (5) and (6). The assumption of coupling forces of the above type thus yields the same intensity distribution as the theory of impact broadening, and at the same time a shift of the whole line, or statistically, both shift and asymmetric broadening. But this result is, so far as the coupling forces are concerned, of a merely heuristic value.

The following possibilities would require further investigation. The quantum mechanical exchange forces can be described by equations of a form similar to

$$(23)\quad \begin{aligned} \dot{q}_1 - (i\omega_1 - x_1)\,q_1 + a\dot{q}_2 - ib'q_2 &= F'(t)\\ a\dot{q}_1 - ib'q_1 + \dot{q}_2 - i\omega_2'q_2 &= F'(t)\end{aligned}$$

where

$$(24)\quad \omega_2' = (\omega_1^2 + \omega_2^2)\frac{1}{2\omega_1},\quad b' = \tfrac{1}{2}\left(a\omega_1 + \frac{b}{\omega_1}\right) + ik,\quad F' = \frac{F}{2\omega_1}$$

The equations (23) lead to the same results as the second order equations (13). It is thus possible that the influence of the assumed coupling forces $k\dot{q}$ and $a\ddot{q}$ indicates a similar influence of the exchange forces.

Suppose the observed line width is partially due to the coupling forces $k\dot{q}$. In this case, since the shift is of the same order of magnitude as the line width

$$|\,(a\omega^2 - b)^2 - k^2\omega^2\,| \sim |\,k\omega\,(a\omega^2 - b)\,|$$

hence also

$$(25)\quad |\,k\omega\,| \sim |\,a\omega^2 - b\,|$$

If, further, $a\omega^2$ and b were of the same order of magnitude, their difference might be comparatively small. In this case the violet shift, $+\frac{1}{2}Hk^2\omega$, could be greater than the red shift, $-\frac{1}{2\omega_1}H\,(a\omega_1^2 - b)^2$. This consideration suggests that perhaps the exchange forces, which are most important for hydrogen and helium, might be responsible for the violet shift, produced frequently by these gases. Heavy gases, on the contrary, for which, certainly, the ordinary electrostatic forces are of decisive importance, always produce red shift.

Classical principles suggest another possibility. Suppose $\sum_{i,j}^{n} a_{ij}\,\dot{q}_i\dot{q}_j$ can

be considered as part of the kinetic energy of the coupled system. For variable coupling coefficients a_{ij} we obtain then

(26) $k_{ij} = \dot{a}_{ij} \sim \nabla\, a_{ij} \cdot v$

where v is the relative velocity of the atoms or molecules considered. Since k is proportional to v, the violet shift, $\frac{1}{2}Hk^2\omega$, would be greater for light than for heavy gases, as is actually the case.

If, as this consideration suggests, the changes of the coupling coefficients were of essential importance, our previous assumption that they are approximately constant, is no longer justified, The general case of equations with variable coefficients will be considered in the next section.

III.

The differential equations of vibrating systems with not too rapidly variable coefficients can be solved by successive approximation. Before resuming our former problem we consider the equation

(27) $\ddot{q} + 2\,[x + x'\,(t)]\,\dot{q} + \omega_0^2\left(1 + \frac{\epsilon(t)}{\omega_0}\right) q = F(t)$

where $\omega_0\sqrt{1+\epsilon(t)/\omega_0}$ is the variable frequency and $x'(t)$ the additional transition probability, which may assume both positive and negative values. If we put

$$q = q_0 + q_1'$$

where q_0 is the solution of the unperturbed equation, we obtain

$$\ddot{q}_1' + 2\,[x + x'(t)]\,\dot{q}_1' + \omega_0\,[\omega_0 + \epsilon(t)]\,q_1' = -\,2x'(t)\,\dot{q}_0 - \omega_0\,\epsilon(t)\,q_0$$

Similarly

$$q_n' = q_n + q_{n+1}'$$

q_n being a solution of

$$\ddot{q}_n + 2x\dot{q}_n + \omega_0^2 q_n = -\,2x'(t)\,\dot{q}_{n-1} - \omega_0\,\epsilon(t)\,q_{n-1}$$

and

(28) $q(t) = \sum_{i=0}^{\infty} q_i(t)$

provided that this series is convergent. The equation for $q_n(t)$ can be solved with the help of Fourier's integral theorem. Suppose $q_{n-1}(t)$ is known, then

(29) $q_n(\omega) = \dfrac{1/2\pi}{\omega^2 - 2ix\omega - \omega_0^2} \int_{-\infty}^{+\infty} [2x'(t)\,\dot{q}_{n-1}(t) + \omega_0\,\epsilon(t)\,q_{n-1}(t)]\,e^{-i\omega t}\,dt$

and

(30) $q_n(t) = \int_{-\infty}^{+\infty} q_n(\omega)\,e^{i\omega t} d\omega$

The negative imaginary part of

$$q(\omega) = \sum_{i=0}^{\infty} q_i(\omega)$$

yields the intensity distribution (v. 19).

If we want to obtain concrete results, we have to use appropriate functions for $x'(t)$ and $\epsilon(t)$. The most easily integrable function of the type required to describe variations of the frequency and transition probability during collisions is $P(t)\, e^{-t^2/\tau^2}$, $P(t)$ being a polynomial. τ is of the order of magnitude of the time during which the coupling interaction is strong. We assume for instance

$$(31)\quad x'(t) = \sum_i \left[x_{0i} + x_{1i} \frac{t - t_i}{\tau_i} + x_{2i} \frac{(t - t_i)^2}{\tau_i^2} \right] e^{-(t-t_i)^2/\tau_i^2}$$

$$(32)\quad \epsilon(t) = \sum_i \left[\epsilon_{0i} + \epsilon_{1i} \frac{t - t_i}{\tau_i} + \epsilon_{2i} \frac{(t-t_i)^2}{\tau_i^2} \right] e^{-(t-t_i)^2/\tau_i^2}$$

t_i being the moment of strongest interaction for the i-th collision. An expression for $q_1(\omega)$ is readily obtained. With the same assumptions as above (15 f. f.) we have

$$q_0(\omega) = F(\omega_0) \frac{1}{\omega_0^2 + 2ix\omega - \omega^2}$$

Integrating by complex variables we get (v. 30)

$$(33)\quad q_0(t) = -\frac{2\pi}{\omega_1} \cdot iF(\omega_0)\, e^{(i\omega - x)t}$$

and with this function from (29)

$$q_1(\omega) = F(\omega_0) \int_{-\infty}^{+\infty} \frac{1}{\omega^2 - \omega_0^2 - 2\, ix\omega} \left[(x_0 - i\epsilon_0) + (x_1 - i\epsilon_1) \frac{t}{\tau} + (x_2 - i\epsilon_2) \frac{t^2}{\tau^2} \right] \times e^{-i(\omega_0 - \omega)\, t - x\, t - t^2/\tau^2}\, dt$$

if for simplicity only one collision is considered, for which $t_i = 0$. Integrating we obtain

$$(34)\quad q_1(\omega) = F(\omega_0) \cdot \frac{\tau\sqrt{\pi}}{2} \left\{ 2 \frac{(x_0 + x_2/4) - i(\epsilon_0 + \epsilon_2/4)}{\omega - \omega_0 - ix} - i\tau(x_1 - i\epsilon_1) - \tfrac{1}{2}\tau^2 (\omega - \omega_0 - ix)(x_2 - i\epsilon_2) \right\} \times \exp\left[-\frac{\tau^2}{4} (\omega - \omega_0)^2 + i \frac{\tau^2 x}{2} (\omega - \omega_0) \right]$$

We consider at first the dependence of the intensity distribution upon x_1 and ϵ_1,

$$(35)\quad J_1(\omega) = \text{Const.} \times \tau \left[x_1 \cos(\omega - \omega_0) \frac{\tau^2 x}{2} + \epsilon_1 \sin(\omega - \omega_0) \frac{\tau^2 x}{2} \right] \times e^{-\frac{\tau^2}{4}(\omega - \omega_0)^2}$$

Negative and positive values of the frequency displacement

$$\Delta\omega \cong \tfrac{1}{2}\, t\, \epsilon_1\, e^{-t^2/\tau^2}$$

are in this case equally probable and the statistical distribution of the frequencies is symmetric. Nevertheless the actual intensity distribution is asymmetric, as is evident from the term containing ϵ_1 in (35). The statement that the method, based upon the Fourier analysis of the frequency variation,[10] "is inadequate for handling shifts and asymmetries...",[2] is thus not necessarily true. This possibility ought to be considered in some cases, for instance, when observed asymmetries, other causes being excluded, are attributed to an unresolved hyperfine structure.[11]

The formula for the intensity distribution derived from (34), is simplified, if x represents only the radiation damping, $x \sim 10^8$ sec.$^{-1}$. For τ is probably of the order of magnitude of the time during which the distance of two colliding atoms is smaller than $\sim 10^{-7}$ cm. Thus $\tau \sim 10^{-11} - 10^{-13}$ sec., and $\tau x \ll 1$. From the exponential term in (34) it is further evident that absorption is perceptible only in a frequency interval where $|\omega - \omega_0|\,\tau \sim 1$, and therefore also $\left|(\omega-\omega_0)\frac{x\tau^2}{2}\right| \ll 1$. The cosine of this expression can thus be replaced by 1, and the sine omitted. We obtain in this case the intensity distribution

$$(36)\quad J(\omega) = \text{Const.}\left\{\frac{x}{(\omega-\omega_0)^2+x^2}\right. +$$

$$\tau\sqrt{\pi}\times\left[2\,\frac{-x\,(x_0+x_2/4)+(\omega-\omega_0)\,(\epsilon_0+\epsilon_2/4)}{(\omega-\omega_0)^2+x^2}\right.$$

$$\left.\left. + \tau x_1 + \tfrac{1}{2}\tau^2\{(\omega-\omega_0)\,\epsilon_2 - x\,x_2\}\right]\times e^{-\frac{\tau^2}{4}(\omega-\omega_0)^2}\right\}$$

In the general case of many collisions we obtain instead of (34) a sum over expressions of the same type with $\left(\frac{\tau_i^{\,2}x_i}{2} - t_i\right)$ instead of $\frac{\tau^2 x}{2}$. If we assume for simplicity $\tau_i = \tau$, $x_{0i} = x$, etc., we have to consider the sums

$$(37)\quad \sum_i \cos(\omega-\omega_0)\left[\frac{\tau^2 x}{2} - t_i\right] = \sum_i \cos(\omega-\omega_0)\,t_i$$

$$(37')\quad \sum_i \sin(\omega-\omega_0)\left[\frac{\tau^2 x}{2} - t_i\right] = \sum_i \sin(\omega-\omega_0)\,t_i$$

The terms containing $\sin(\omega-\omega_0)\frac{\tau^2 x}{2}$ are omitted as above and $\cos(\omega-\omega_0)\times\frac{\tau^2 x}{2}$ is replaced by 1. The sum over the sines becomes very small, when many collisions are taken into account, since both negative and positive values of the terms are equally probable. We may expect that the

calculation of (37) by means of statistical methods will lead to a function of ω, containing as a parameter the mean time between two successive collisions, say T, and decreasing for $|\omega - \omega_0| > \frac{2\pi}{T}$. Denoting this function by $f(\omega,T)$, we shall have (v. 36)

$$(38)\quad J(\omega) = \text{Const.} \times \left[\frac{x}{(\omega - \omega_0)^2 + x^2} + f(\omega, T)\, \tau \sqrt{\pi}\, \{c.\,(36)\}\, e^{-\frac{\tau^2}{4}(\omega-\omega_0)^2} \right]$$

The function $f(\omega, T)$ represents the ordinary impact broadening; but with our assumptions there is no indication that $\frac{1}{T}$ could be simply added to x as in Lorentz' theory of impact broadening where it determines the line width directly. Our results show that not only T, as has been assumed hitherto, but also τ and the type of the collision process are of considerable, if not decisive, importance for the intensity distribution.

Equations (13) with variable coefficients can be solved in a similar way. We assume

$$(39)\quad \begin{aligned} a(t) &= (a_0 + a_1 t/\tau)\, e^{-t^2/\tau^2} \\ b(t) &= (b_0 + b_1 t/\tau)\, e^{-t^2/\tau^2} \\ k(t) &= (k_0 + k_1 t/\tau)\, e^{-t^2/\tau^2} \end{aligned}$$

From the solution for uncoupled vibrators

$$q_{10} = e^{i\omega_1^* t}, \qquad q_{20} = 0$$

where for simplicity the amplitude constant has been omitted and $\omega^* = \omega + ix$ we obtain as before (v. 29)

$$q_{21}(\omega) = \frac{\frac{1}{2}\pi}{\omega_2^2 - \omega^2} \int_{-\infty}^{+\infty} [a(t)\, \ddot{q}_{10} + k(t)\, \dot{q}_{10} + b(t)\, q_{10}]\, e^{-i\omega t} dt$$

and integrating

$$q_{21}(\omega) = \frac{\tau H}{\sqrt{\pi}} [A_0 + \tfrac{1}{2} i\tau (\omega_1^* - \omega)\, A_1] \times e^{-\frac{\tau^2}{4}(\omega_1^* - \omega)^2}$$

where

$$\begin{aligned} A_0 &= a_0 \omega_1^{*2} - i k_0 \omega_1^* - b_0 \\ A_1 &= a_1 \omega_1^{*2} - i k_1 \omega_1^* - b_1 \end{aligned}$$

and within the narrow frequency interval considered

$$H = \frac{1}{\omega_2^2 - \omega^2} \cong \frac{1}{\omega_2^2 - \omega_1^2}$$

We obtain further (v. 30)

$$(40)\quad \begin{aligned} q_{21}(t) &= \int_{-\infty}^{+\infty} q_{21}(\omega)\, e^{i\omega t} d\omega \\ &= 4H\, (A_0 + A_1 t/\tau)\, e^{-\frac{t^2}{\tau^2}}\, q_{10}(t) \end{aligned}$$

If $\frac{1}{\tau} \ll \omega$, we obtain a sufficient approximation, putting

$$\dot{q}_{21} = i\omega^* q_{21}(t), \qquad \ddot{q}_{21} = -\omega_1^{*2} q_{21}(t)$$

in the first of equations (13), which becomes

$$(41)\quad \ddot{q}_1 + x\dot{q}_1 + [\omega_1^2 + \epsilon(t)\,\omega_1]\, q_1 = \mathrm{F}(t)$$

with

$$(42)\quad \epsilon(t) = -\,4\mathrm{H}/\omega_1 \times (\mathrm{A}_0 + \mathrm{A}_1 t/\tau)^2\, e^{-t^2/\tau^2}$$

If we wish to consider only the asymmetries, we can omit the imaginary part of $\epsilon(t)$, which describes the variation of the transition probability and indicates symmetric broadening. Comparing the real part of (42) and (32), we see that

$$(43)\quad \begin{cases} \epsilon_0 = \dfrac{4\mathrm{H}}{\omega_1}[(a_0\,\omega_1^2 - b_0) - k_0^2\,\omega_1^2)] \\ \epsilon_1 = 0 \\ \epsilon_2 = \dfrac{4\mathrm{H}}{\omega_1}[(a_0\,\omega_1^2 - b_0) - k_0^2\,\omega_1^2)] \end{cases}$$

We obtain thus for the asymmetric part of the intensity distribution (v.36,38)

$$(44)\quad \mathrm{J}_a(\omega) = \text{Const.} \times f(\omega, \mathrm{T}) \times \left\{ \frac{2\,(\omega_1-\omega)\,[(a_0\omega_1^2-b_0)^2-k_0^2\omega_1^2]}{(\omega_1^2-\omega)^2+x^2} + \tfrac{1}{2}\,\tau^2\,(\omega_1-\omega)\,[(a_1\omega_1^2-b_1)^2-k_1^2\,\omega_1^2] \right\} e^{-\frac{\tau^2}{4}(\omega-\omega_2)^2}$$

It is evident from this formula that the asymmetric broadening and the shift of spectral lines agree as to their sign with the frequency displacement (6), which has been calculated for constant coupling forces. It seems, however, that the form of spectral lines is chiefly determined by the way in which the coupling forces vary with time. We see that the influence of the assumed coupling forces, as expressed by the functions $a_0\, e^{-t^2/\tau^2}..$, and $a_1\, t/\tau \times e^{-t^2/\tau^2}..$, is quite different. The former determine the intensity distribution chiefly in the central parts of the spectral line and the latter in the wings. These results indicate that it may be possible to derive some conclusions concerning the nature of the interaction forces from the form of spectral lines.

The assumed generalisation of coupling forces leads, as we have seen, to results which are in qualitative agreement with experiment. But we have still to investigate, whether formulæ, analogous to that obtained for the red shift (11), can be also obtained for the width and the violet shift of spectral lines; and, further, we have to represent the interactions by the proper functions of time, so that the formulæ for the intensity distribution could be tested experimentally.

REFERENCES.

1. Margenau .. .. *Phys. Rev.*, 1932, **40**, 387.
2. „ .. .. *Phys. Rev.*, 1935, **48**, 755.
3. Holtsmark .. .. *Zeits. f. Phys.*, 1925, **34**, 722.
4. Mensing .. .. *Zeits. f. Phys.*, 1925, **34**, 611.
5. „ .. .. *Zeits. f. Phys.*, 1930, **61**, 655.
6. Frenkel .. .. *Zeits. f. Phys.*, 1930, **59**, 198.
7. Hasche, Polanyi and Vogt *Zeits. f. Phys.*, 1926, **41**, 497.
8. Fermi .. .. *Cim.*, 1934, **11**, 157.
9. Reinsberg .. .. *Zeits. f. Phys.*, 1935, **93**, 416.
10. Weisskopf .. .. *Phys. Zeits.*, 1933, **34**, 1.
11. Minkowski .. .. *Zeits. f. Phys.*, 1935, **95**, 284.

ULTRASONIC VELOCITIES IN SOME ORGANIC LIQUIDS—PART II.

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1. Introduction.

In a paper appearing in the *Proceedings of the Indian Academy of Sciences*, Vol. II, p. 497 (1935), the author gave determinations of ultrasonic velocities in 52 organic liquids. It was thought that it would be of interest to find out the velocities in some related groups of organic liquids. In the present paper, results of both ultrasonic velocities and adiabatic compressibilities are given for di-esters, for the xylenes and for two bases, quinoline and *o*-toluidine.

The complete experimental arrangement has been described in the earlier paper.*

In these experiments, the liquids which were distilled, were contained in a cubic glass cell of 100 c.c. capacity, bigger than the vessel used previously. They were all of the purest stock, from Kahlbaum or Merck or Dr. Schukardt or de Haen.

The frequency employed for the vibration was $7 \cdot 37 \times 10^6$ cycles per second. The temperatures at which the determinations were made, are noted against each liquid.

2. Results.

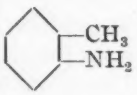
The following table contains the results of determinations of ultrasonic velocities in 14 organic liquids. The last column gives the calculated adiabatic compressibilities from the known acoustic velocities.

* In a private communication to the author, Professor J. C. Hubbard has explained the two points raised in the earlier paper on page 504.

TABLE I. *Ultrasonic velocities at* $7 \cdot 37 \times 10^6$ *cycles/second.*

Liquids	Chemical Formula	Temp. in °C.	Wave-length of sound in mms.	Velocity of sound in meters per second	Adiabatic compressibility $\beta\phi \times 10^6$
o-Xylene	$C_6H_4(CH_3)_2$	22°	0·1834	1352	62·4
m-Xylene	,, ,,	22°	0·1800	1328	65·9
p-Xylene	,, ,,	22°	0·1805	1330	65·9
Diethyl oxalic ester	$\begin{matrix}COO\cdot C_2H_5\\ \vert\\ COO\cdot C_2H_5\end{matrix}$	22°	0·1888	1392	48·0
Diethyl malonic ester	$CH_2\begin{matrix}\diagup COO\cdot C_2H_5\\ \diagdown COO\cdot C_2H_5\end{matrix}$	22°	0·1879	1386	49·6
Diethyl succinic ester	$\begin{matrix}CH_2-COOC_2H_5\\ \vert\\ CH_2-COOC_2H_5\end{matrix}$	22°	0·1869	1378	50·7
Diethyl adipic ester	$\begin{matrix}CH_2\cdot CH_2\cdot COOC_2H_5\\ \vert\\ CH_2\cdot CH_2\cdot COOC_2H_5\end{matrix}$	22°	0·1866	1376	52·7
Diglycollic ester	$O\begin{matrix}\diagup CH_2\cdot COOC_2H_5\\ \diagdown CH_2\cdot COOC_2H_5\end{matrix}$	22°	0·1947	1435	43·9
Thiodiglycollic ester	$S\begin{matrix}\diagup CH_2\cdot COOC_2H_5\\ \diagdown CH_2\cdot COOC_2H_5\end{matrix}$	22°·5	0·1966	1449	41·7
Methyl adipate	$\begin{matrix}CH_2\cdot CH_2\cdot COO\cdot CH_3\\ \vert\\ CH_2\cdot CH_2\cdot COO\cdot CH_3\end{matrix}$	21°·8	0·1994	1469	43·9

TABLE I—(*contd.*)

Liquids	Chemical Formula	Temp. in °C.	Wave-length of sound in mms.	Velocity of sound in meters per second	Adiabatic compressibility $\beta\phi \times 10^6$
Acetone dicarboxylic ester	$CO\begin{matrix}CH_2\cdot COO\cdot C_2H_5\\ CH_2\cdot COO\cdot C_2H_5\end{matrix}$	22°·5	0·1828	1348	50·7
Quinoline		22°	0·2228	1643	34·0
o-Toluidine		22°·5	0.2265	1669	36·1
Methyl hexaline	$C_6H_{10}(CH_3)$ (OH)	22°	0·1936	1428	53·7

Of the liquids studied here, data of previous determinations are available only for four liquids. We give below, in Table II, values for comparison with those obtained earlier.

TABLE II.

Velocities in meters/second.

Liquids	Audio range from I. C. T.	R. Bär. Freq. about $7\cdot5\times10^6$ c./s.	Author Freq. $7\cdot37\times10^6$ c./s.
o-Xylene	—	1345 at 21° C.	1352 at 22° C.
m-Xylene	—	1330 at 21° C.	1328 ,, ,,
p-Xylene	—	1333	1330 ,, ,,
o-Toluidine	1645 at 21° C.	—	1669 ,, 22°·5 C.
m-Toluidine	1602·4 at 21°·6 C.	—	—

R. Bär's results are taken from a paper by him appearing in *Helv. Phys. Acta* 1933, **6**, 578 ; while for the audio range, the value for *o*-toluidine is taken from the *International Critical Tables*. The velocity for *m*-xylene has already been given in the earlier paper. The results are in good agreement.

3. *Discussion.*

Remarks of a general kind were made in the earlier paper, of the relation between sound velocities and chemical constitution. We shall, however, go more elaborately in this paper.

The xylenes : The sound velocity in the ortho-compound is higher than in the other two xylenes which have approximately the same velocities. Substitution in the ortho position favours greater sound velocity. Even for the toluidines, ortho has the higher velocity (see Table II).

The di-esters (ethyl): In the series, oxalic, malonic, succinic and adipic esters, the sound velocity decreases with increasing weights of the radical. The same effect was noticed in the earlier paper, on the ethyl esters of formic, acetic, propionic and butyric acids. In the latter group, ethyl formate has a velocity of 1263 m./s., those for the remaining compounds being 1187, 1185 and 1171 m./s. respectively. This is quite the reverse of what obtains in hydrocarbons and alcohols ; the sound velocity increasing with the length of the chain.

Ethyl and methyl adipates: Introduction of a methyl radical instead of an ethyl radical in an ester, enhances the sound velocity. That this is true can be seen from the earlier results also, given below :

Liquids	Velocity of sound in meters/second
Ethyl adipate	1376
Methyl ,,	1469
Ethyl acetate	1187
Methyl ,,	1211
Ethyl propionate	1185
Methyl ,,	1215

In all the cases above given, even though the length of the chain increases, by the introduction of an ethyl in place of a methyl radical, there is a decided diminution in velocity. Variations in density alone cannot account for this anomaly.

Thio- and di-glycollic esters : In the thio-compound an atom of sulphur replaces an atom of oxygen in the diglycollic ester. The velocity is enhanced in the thioglycollic ester. But it was observed in the earlier paper that the introduction of a heavy atom usually lowered the sound velocity ; *cf.* carbon tetrachloride and chloroform ; methylene chloride and methylene bromide. When we find that the esters behave differently from alcohols or hydrocarbons in the matter of velocity of sound, and when we know that we are now dealing with these two esters, it is not difficult to understand why it should be so.

o-toluidine and quinoline : The ultrasonic velocity in *o*-toluidine is much higher than that for toluene, but nearer to that of aniline ; to which it is related, being less by about 15 meters. Quinoline, another base, has a velocity higher than that for either pyridine or benzene. Bases usually show higher sound velocities than the corresponding hydrocarbons.

The author thanks Sir C. V. Raman, Kt., for his interest in the work.

Summary.

The paper contains determinations of ultrasonic velocities in 14 organic liquids, some of them being di-esters, by the method of diffraction of light by high frequency sound waves. Included are also adiabatic compressibilities for these compounds, calculated therefrom.

PHYSICAL PRINCIPLES AND APPLICATIONS OF MAGNETO-CHEMISTRY
by Prof. S. S. Bhatnagar and Dr. K. N. Mathur.

By C. V. Raman.

It has long been familiar to chemists that optical properties such as refraction, dispersion and optical activity furnish very useful indications of molecular constitution. The importance of the study of dielectric behaviour and the significance of the electric moment of the molecule has also of late been appreciated by workers in the field of chemistry. The fundamental importance of studies of magnetic behaviour from a chemical point of view has not, however, received the same degree of general recognition, and this may in part be due to the lack of suitable texts dealing specially with magneto-chemistry. Van Vleck's "Electric and Magnetic Susceptibilities" (1932) in which the theoretical aspects of magnetism are handled in a masterly manner is accessible only to one fairly well equipped with mathematical knowledge. E. C. Stoner's "Magnetism and Matter" (1934) is less severely mathematical and devotes more space to the experimental aspects of the subject and is consequently within the reach of a wider circle of readers. There remained nevertheless a distinct need for a book addressed primarily to the chemist and dealing with magnetism from the chemical standpoint; and it may be said at once that this gap has been satisfactorily filled by the book now under review.

The book has several pleasing features. It covers the field in an adequate manner and presents the subject in the proper historical perspective. It includes an account of experimental methods which should be useful to the intending researcher, and sufficient theory to form at least a beginning to a deeper knowledge of the subject. There are useful tables of data and adequate references to the literature. The treatment endeavours to be critical without being unduly severe on opinions or statements with which the authors disagree. The classical investigations, and the latest researches alike receive their due share of attention. It is specially pleasing to notice the numerous references to work done at various centres of research in India in the subject, but the space given to such references does not appear to be greater than the intrinsic importance of the contributions referred to demands. Taken altogether, the book is a production which does great credit to the

authors and will, it is hoped, be widely used. It is easy to see that the authors are thoroughly familiar with their subject, as might well be expected from the fact that their own original contributions are significant in volume and quality. It is some satisfaction to find that the leading Indian investigators, such as the writers of this book, are entering the field of authorship as producers of advanced scientific treatises. It is difficult and laborious work but is very necessary for gaining recognition for themselves and for Indian centres of learning as sources of new knowledge.

A perusal of the book indicates that there is yet an immense field of research awaiting the explorer in magneto-chemistry. There is much to be done before the mass of empirical experience in the magnetic behaviour of the ferrous metals and their alloys is reduced to a coherent body of knowledge. In the study of para- and dia-magnetic susceptibilities and their variations with physical condition and chemical constitution, there is an almost illimitable territory of research. The study and interpretation of magne-crystallic action, both of dia- and of para-magnetic compounds such as is being pursued with success by K. S. Krishnan and his collaborators at Calcutta, promises results of real importance. The remarkable differences in the magnetic character and anisotropy of the molecules of the aliphatic and aromatic compounds disclosed by recent investigations are obviously connected with the deepest problems of organic chemistry. It is greatly to be hoped that these will be further studied and elucidated.

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